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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21C 5/02	A1	(11) International Publication Number: WO 96/31646 (43) International Publication Date: 10 October 1996 (10.10.96)									
<p>(21) International Application Number: PCT/JP96/00942</p> <p>(22) International Filing Date: 5 April 1996 (05.04.96)</p> <p>(30) Priority Data:</p> <table border="0"><tr><td>7/80403</td><td>5 April 1995 (05.04.95)</td><td>JP</td></tr><tr><td>7/80404</td><td>5 April 1995 (05.04.95)</td><td>JP</td></tr><tr><td>7/80405</td><td>5 April 1995 (05.04.95)</td><td>JP</td></tr></table> <p>(71) Applicant (for all designated States except US): KAO CORPORATION [JP/JP]; 14-10, Nihonbashi-Kayabacho 1-chome, Chuo-ku, Tokyo 103 (JP).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): IRINATSU, Yuichi [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). MIYAUCHI, Yoshitaka [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). TAKAHASHI, Hiromichi [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP).</p> <p>(74) Agents: FURUYA, Kaoru et al.; Nihonbashi TM Building, 1-8-11, Nihonbashi-Horidomecho, Chuo-ku, Tokyo 103 (JP).</p>		7/80403	5 April 1995 (05.04.95)	JP	7/80404	5 April 1995 (05.04.95)	JP	7/80405	5 April 1995 (05.04.95)	JP	<p>(81) Designated States: CA, CN, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: DEINKING METHOD</p> <p>(57) Abstract</p> <p>A deinking method comprising the steps of liberating ink from a waste paper as a raw material and removing the liberated ink from a flotation system, wherein a nonionic surfactant, e.g., a reaction product obtained by adding an alkylene oxide to a mixture of an oil and fat and an alcohol, an alkylene oxide adduct of a fatty acid, or an alkylene oxide adduct of a higher alcohol, is used for the liberation of ink, and the flotation step is effected in the presence of a cationic compound, an amine, an acid salt of an amine or an amphoteric compound at a pH of from 4 to 9, provides a high quality deinked pulp having a high whiteness and a little residual ink spots.</p>											

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DESCRIPTION

DEINKING METHOD

Background of the Invention

Field of the Invention

The present invention relates to a deinking method for deinking waste papers such as news papers, leaflets and magazines to reclaim them. More particularly, it relates to a deinking method excellent in workability by which an excellent deinked pulp having a higher whiteness and a less residual ink spots is obtained at a high yield.

Description of the Related Art

Waste papers are reclaimed by liberating ink from the waste papers by a deinking treatment to prepare reclaimed pulp and manufacturing reclaimed paper from the reclaimed pulp. The conventional deinking method generally comprises a step of liberating ink from waste papers and another step of rejecting the liberated ink.

More specially, the deinking method comprises, as main steps,

- (1) a step of pulping (disintegrating) waste papers,
- (2) a step of aging, i.e., leaving the disintegrated

paper as it is.

(3) a step of flotation, and

(4) a step of washing.

That is, in deinking treatment, ink bound to the fibers of waste papers is physically and chemically (or biochemically) liberated therefrom to thereby separate the ink from the fibers. Thus, reclaimed pulp is obtained.

In effecting deinking treatment, a deinking agent comprising a surfactant such as a polyoxyethyl alkyl ether and a fatty acid is generally used in any of the above-described steps, for the purposes of liberating ink from waste papers or generating foams to which the liberated ink will adhere.

In recent years, the properties of waste papers which are used as raw materials have been varied because of an increase in a demand for a beautiful and stable printing and a progress in printing techniques. In addition, degrees of binding of ink to paper are varied, including loose ones and tight ones. Under these circumstances, it is demanded to improve the quality and the recovery (i.e., the productivity) of deinked pulp. In order to attain such a purpose, various proposals are offered from various fields including deinking processes, deinking agents and

apparatuses used for deinking.

In conventional deinking methods, the pulping step and the flotation step are usually carried out at an alkaline pH of exceeding 9, and in an extremely few cases, at a pH of 9 or less. Deinking methods wherein the pulping step and the flotation step are carried out at a pH of 9 or less are disclosed in Japanese Patent Publication-A Nos. 54-23705 and 59-53532, and U.S. Patent No. 4,043,908 (published on Aug. 23, 1977; Assignees: Kemanord Aktiebolag and Sala International AB). Specially, Japanese Patent Publication-A No. 54-23705 discloses a method wherein an aluminum salt or white water is added to a waste paper dispersion, the pH of the dispersion is adjusted to a pH ranging from 4 to 7, a polyelectrolyte is added to the dispersion, and then the flotation is effected. Japanese Patent Publication-A No. 59-53532 discloses that a specific alkylamine polyether, which behave as an amine at a basic pH and as an quaternary ammonium at an acidic pH, contributes to the appearances of foam performances required during the pulping step, deinking step of washing-system and flotation step, respectively. U.S. Patent No. 4,043,908 discloses a method wherein an ethylene oxide adduct of an amine is used for liberating ink from pulp, and the

disintegration of waste papers and the liberation of ink therefrom is carried out at a high pH to thereby introduce the ink into micelles, and then the pH of the system is reduced to break the micelles, thereby separating (precipitating) the ink from the pulp, and the ink is removed out of the system by flotation.

According to the method disclosed in Japanese Patent Publication-A No. 54-23705, however, the lathering power is markedly high, and therefore a decrease in the recovery of pulp and an increase in the amount of foams to be rejected (or discharged) during flotation step occur. Such an excess generation of foams is not preferred for flotation and brings about reductions in productivity and quality. The alkylamine polyether disclosed in Japanese Patent Publication-A No. 59-53532 is inferior to conventional polyoxyethylene alkyl ether type deinking agents in the ink-liberating performance and therefore can not provide a pulp having a high whiteness. Further, the ink liberated from pulp with the use of such an alkylamine polyether is in the form of very fine drops and does not have an optimum size suitable for the adsorption to the foam during flotation. Accordingly, the ink can not sufficiently be removed during flotation. The method disclosed in U.S. Patent No.

4.043.908 does not attain sufficient deinking. The reason is not necessarily clarified, but it is considered to be due to when an ethylene oxide adduct of an amine is used as the deinking agent in the disintegrating step wherein ink is liberated from pulp, the ink is not sufficiently liberated therefrom, and that when the pH of the system is reduced for flotation, the ink which is dispersed in the system or dissolved in the micelles once again adheres to the pulp.

Disclosure of the Invention

Summary of the Invention

Under the above-mentioned circumstances, the present inventors have made extensive investigations from the viewpoint of the deinking method. As a result of the investigations, the present inventors have found that a deinked pulp having a higher whiteness and a less residual ink spots can be obtained by liberating ink sufficiently from waste papers with the use of a nonionic surfactant as a deinking agent, and effecting the flotation step at a pH of from 4 to 9 in the presence of a cationic compound, an amine, an acid salt of an amine or an amphoteric compound. The present invention has been

completed on the basis of this finding.

Thus, the present invention provides a deinking method comprising the steps of liberating ink from waste paper as a raw material and removing the liberated ink from a flotation system, which comprises adding at least one nonionic surfactant for liberating ink from said waste paper; adjusting the pH of a system to pH 4 to 9 before or during said step for removing the liberated ink from a flotation system; and adding at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds before or during said step for removing the liberated ink from a flotation system.

In other word, the present invention relates to a deinking method comprising at least steps of liberating ink from waste paper as a raw material and removing the liberated ink from a flotation system, wherein at least one nonionic surfactant is used for the liberation of ink; and at least part of the flotation step is effected in the presence of at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds at a pH in a range of from 4 to 9.

The nonionic surfactant is preferably selected from the group consisting of nonionic surfactants (A) to (D):

nonionic surfactant (A): a reaction product obtained by adding an alkylene oxide to a mixture of an oil & fat and an alcohol,

nonionic surfactant (B): a compound represented by the formula: $\text{RCOO}(\text{AO})_m\text{R}'$ (wherein R represents an alkyl or alkenyl group having 7 to 23 carbon atoms; R' represents a hydrogen atom, an alkyl group having 1 to 22 carbon atoms, an alkenyl group having 2 to 22 carbon atoms, or an acyl group having 2 to 22 carbon atoms; AO represents an oxyalkylene group having 2 to 4 carbon atoms; and m is an integer of 1 or more),

nonionic surfactant (C): a compound represented by the formula: $\text{RO}(\text{AO})_n\text{H}$ (wherein R represents an alkyl or alkenyl group having 8 to 24 carbon atoms; AO represents an oxyalkylene group having 2 to 4 carbon atoms; and n is an integer of 1 or more), and

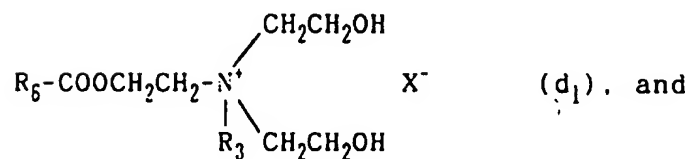
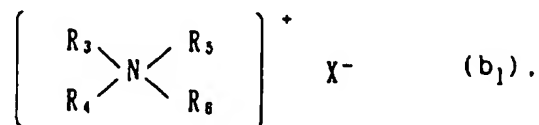
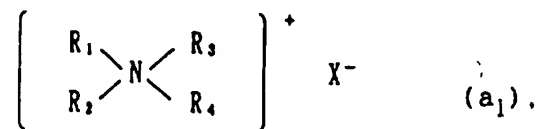
nonionic surfactant (D): a reaction product obtained by adding an alkylene oxide to a polyvalent carboxylic acid or an acid anhydride thereof; or a reaction product obtained by adding an alkylene oxide to a mixture of a polyvalent carboxylic acid or an acid anhydride thereof, and alcohol.

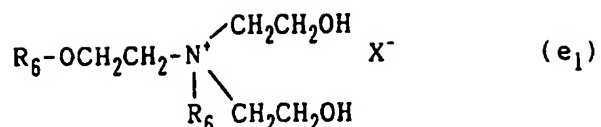
The addition form of alkylene oxides in an alkylene oxide adduct among the nonionic surfactants described above may be a block one or a random one, or alternatively a mixture thereof.

At least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds is desirably added to the flotation system after adjusting the pH of the system to a value in a range of from pH4 to pH9. In this case, at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds is preferably used in an amount such that the pH of the flotation system is scarcely altered by the addition of such at least one member.

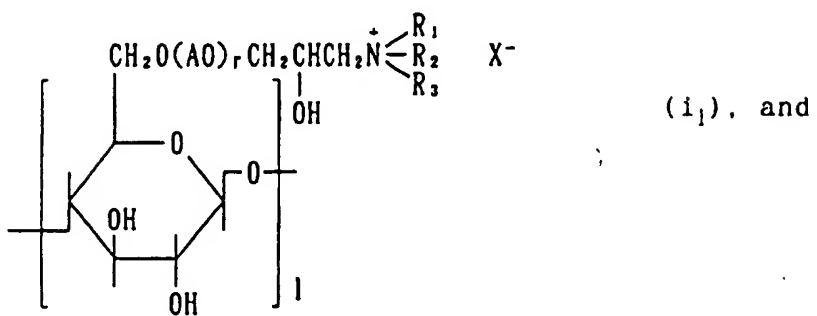
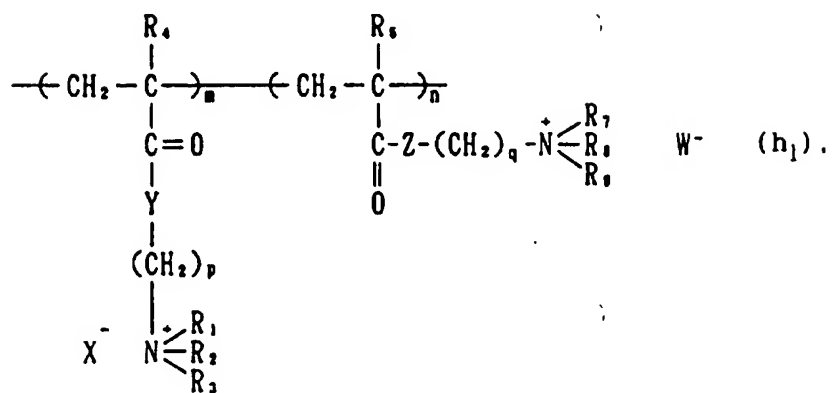
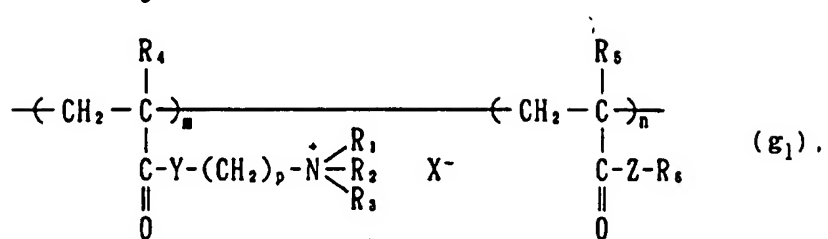
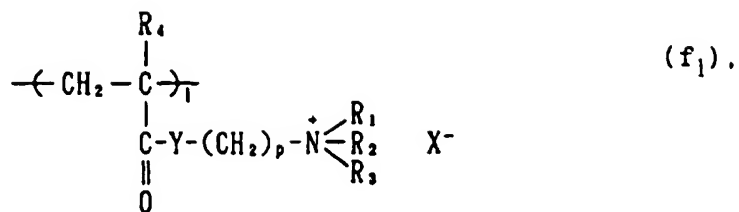
The cationic compounds are desirably selected from the group consisting of compounds represented by the following formulas (a₁) to (e₁) and cationic polymers represented by the following formulas (f₁) to (j₁) each of which has a cationic nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000; the amines and acid salts of amines are desirably selected from the group consisting of compounds represented by the following formulas (a₂) to (h₂) and polymers represented by the

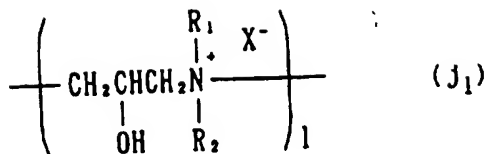
following formulas (i₂) to (l₂) each of which has an amino-nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000; and the amphoteric compounds are desirably selected from the group consisting of compounds represented by the following formulas (a₃) to (j₃), phospholipids (k₃), proteins (l₃) and amphoteric polymers represented by the following formulas (m₃) and (n₃) each of which has a cationic nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000:



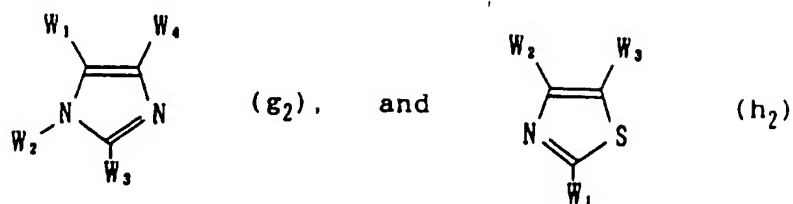
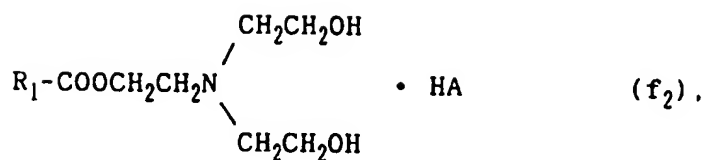
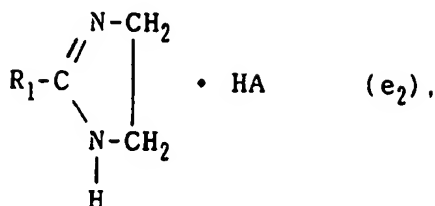
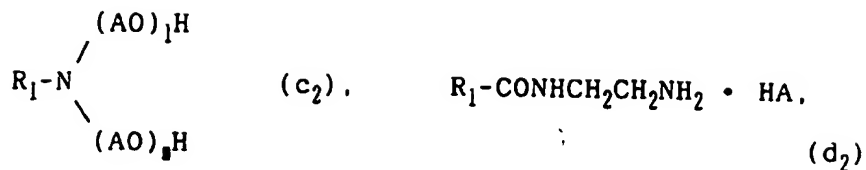
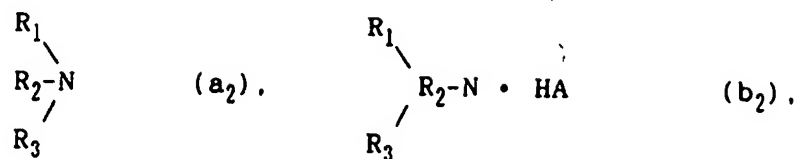


in formulas (a₁) to (e₁), R₁ and R₂ may be the same or different from each other and each represents an alkyl, alkenyl or β-hydroxyalkyl group having 10 to 24 carbon atoms; R₃, R₄ and R₅ may be the same or different from one another and each represents an alkyl or hydroxyalkyl group having 1 to 8 carbon atoms, a benzyl group, or a group represented by the formula: -(AO)_n-Z (wherein AO represents an oxyalkylene group having 2 to 4 carbon atoms, Z represents a hydrogen atom or an acyl group, and n is an integer of from 1 to 50); R₆ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; X⁻ represents a counter ion; and Y represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms, a group represented by the formula: R₆COOCH₂- (wherein R₆ is as defined above), a group represented by the formula: R₆CONHCH₂- (wherein R₆ is as defined above) or a group represented by the formula: R₆OCH₂- (wherein R₆ is as defined above);



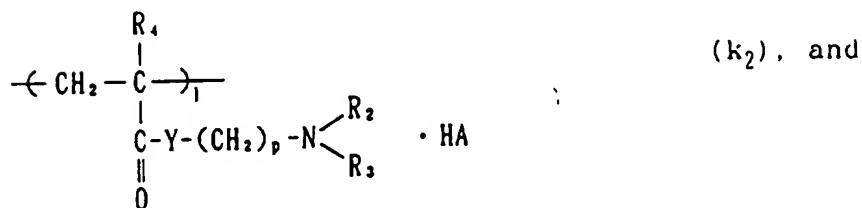
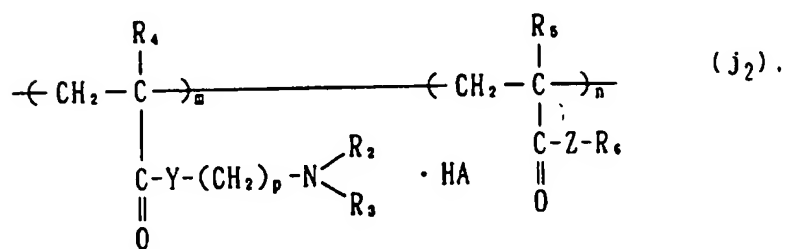
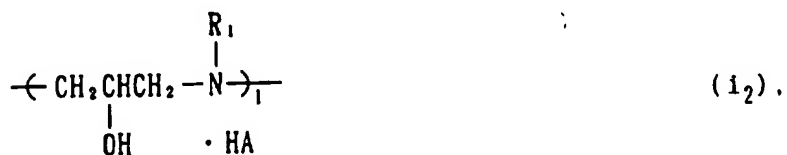


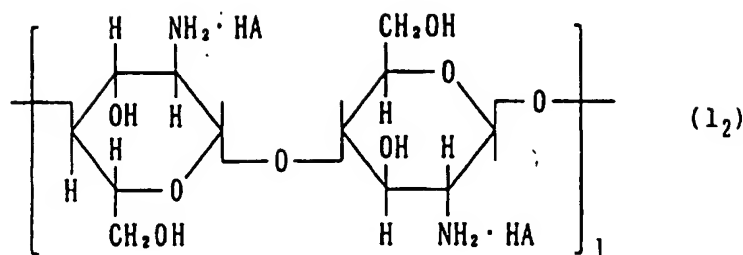
in formulas (f₁) to (j₁), R₁, R₂, R₃, R₆, R₇, R₈ and R₉ may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ and R₅ may be the same or different from each other and each represents a hydrogen atom or a methyl group; X⁻ and W⁻ may be the same or different from each other and each represents a counter ion; Y and Z may be the same or different from each other and each represents O or NH; A0 represents an oxyalkylene group having 2 to 4 carbon atoms; p and q may be the same or different from each other and each represents an integer of 1 to 10; r represents an integer of 0 to 10; and l, m and n are each such a positive number that the weight-average molecular weight of the polymer would be a value in the range of from 2,000 to 3,000,000;



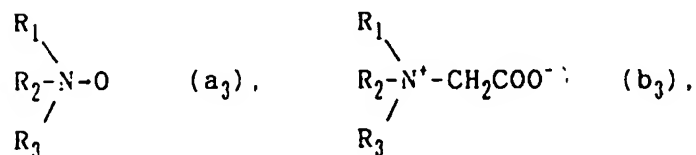
in formulas (a₂) to (h₂), R₁ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; R₂ and R₃ may be the same or different from each other and each represents a

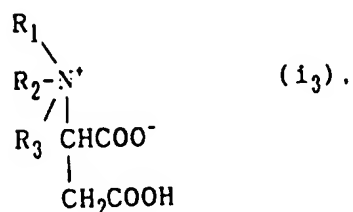
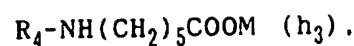
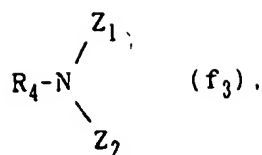
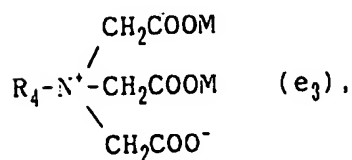
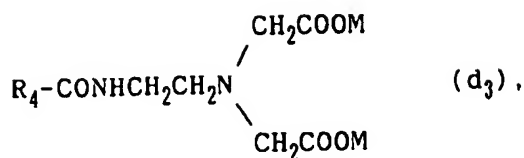
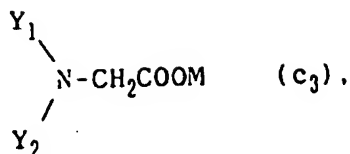
hydrogen atom, an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; HA represents an inorganic or organic acid; AO represents an oxyalkylene group having 2 to 4 carbon atoms; l and m are each zero or a positive integer with the proviso that l plus m is an integer of 1 to 300; and W_1 , W_2 , W_3 and W_4 may be the same or different from one another and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms;



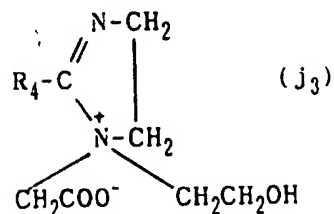


in formulas (1₂) to (1₂), R₁ represents an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₂, R₃ and R₆ may be the same or different from one another and each represents a hydrogen atom, an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ and R₅ may be the same or different from each other and each represents a hydrogen atom or a methyl group; HA represents an inorganic or organic acid; Y represents O or NH; p represents an integer of 1 to 10; and l, m and n are each such a positive number that the weight-average molecular weight of the polymer would be a value in the range of from 2,000 to 3,000,000;



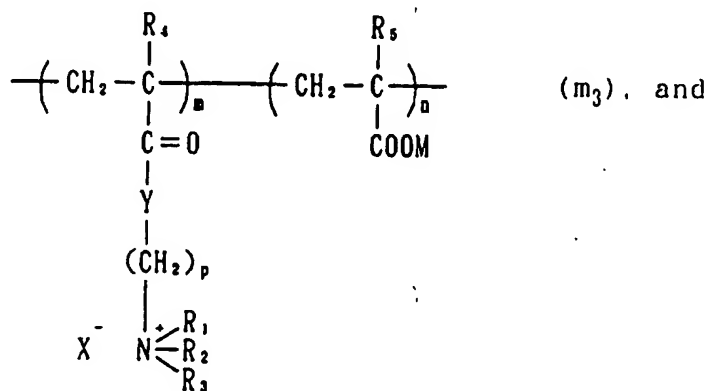


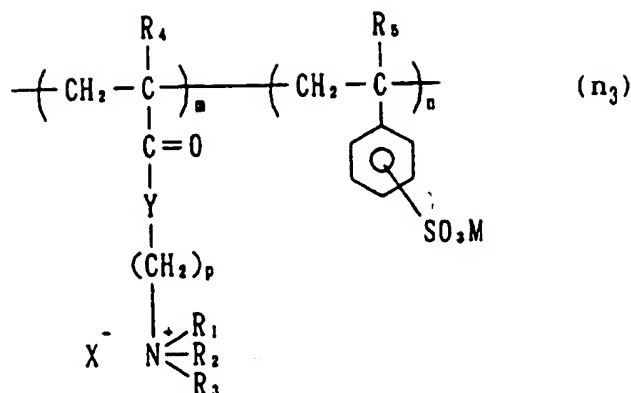
and



in formulas (a₃) to (j₃). R₁, R₂ and R₃ may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; M represents a hydrogen atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an

ammonium group; Y_1 represents a group represented by the formula: $R_5NHCH_2CH_2-$ (wherein R_5 represents an alkyl group having 1 to 36 carbon atoms or an alkenyl or β -hydroxyalkyl group having 2 to 36 carbon atoms); Y_2 represents a hydrogen atom or a group represented by the formula: $R_5NHCH_2CH_2-$ (wherein R_5 is as defined above); Z_1 represents a group represented by the formula: $-CH_2COOM$ (wherein M is as defined above); and Z_2 represents a hydrogen atom or a group represented by the formula: $-CH_2COOM$ (wherein M is as defined above); and



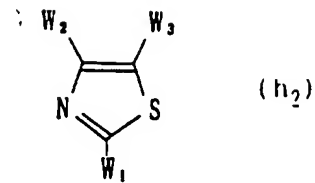
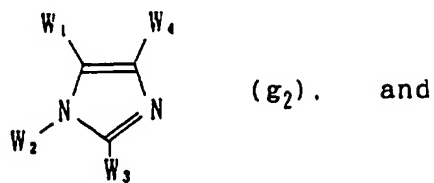
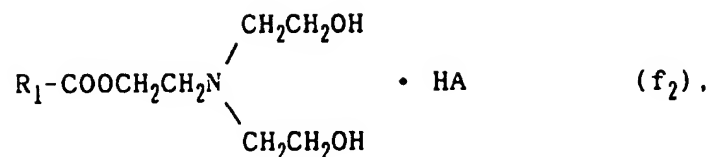
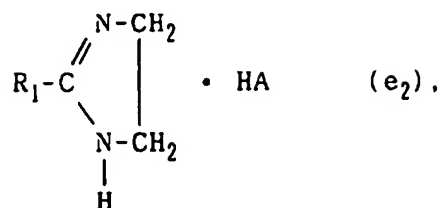
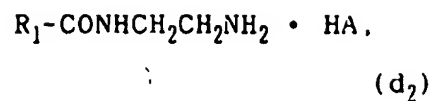
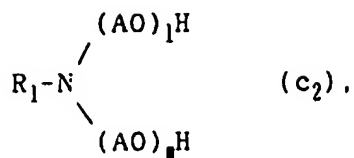
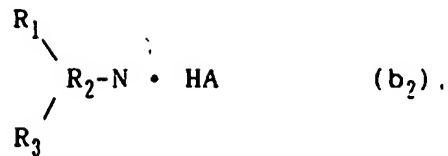
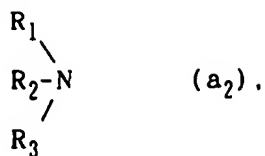


in formulas (m₃) and (n₃), R₁, R₂ and R₃ may be the same or different from one another and each represents a hydrogen atom, an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ and R₅ may be the same or different from each other and each represents a hydrogen atom or a methyl group; M represents a hydrogen atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an ammonium group; X⁻ represents a counter ion; Y represents O or NH; p is an integer of 1 to 10; and m and n are each such a positive number that the weight-average molecular weight of the polymer would be a value in the range of from 2,000 to 3,000,000.

The present invention includes a deinking method comprising at least a step of liberating ink from

waste paper as a raw material and a step of removing the liberated ink therefrom by flotation, characterized in that one or two or more deinking agent(s) selected from among the above nonionic surfactants (A) to (D) is(are) used; the pH in the system during flotation is controlled to 4 to 9; and a cationic compound(s) is(are) allowed to be present in the system during flotation. In this case, the cationic compound(s) is(are) preferably one or more compounds selected from the group consisting of those represented by the above formulas (a₁) to (e₁).

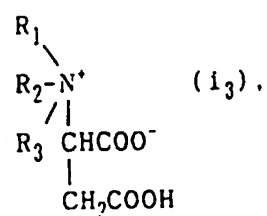
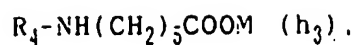
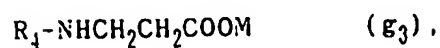
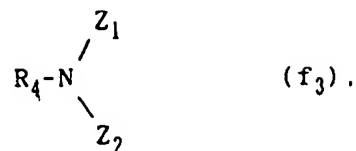
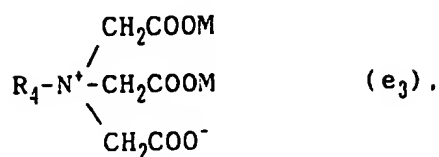
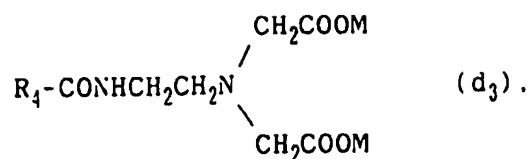
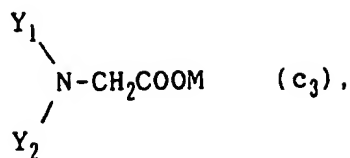
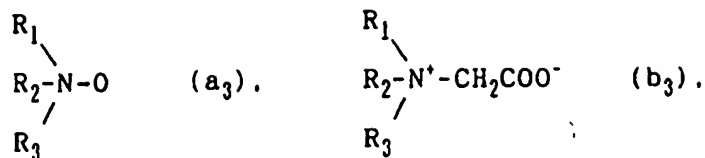
The present invention also includes a deinking method comprising at least a step of liberating ink from waste paper as a raw material and a step of removing the liberated ink therefrom by flotation, characterized in that one or two or more deinking agent(s) selected from among the above nonionic surfactants (A) to (D) is(are) used; the pH in the system during flotation is controlled to 4 to 9; and an amine(s) or an acid salt(s) of an amine(s) is(are) allowed to be present in the system during flotation. In this case, the amine(s) or the acid salt(s) of the amine(s) is(are) preferably one or more compounds selected from the group consisting of those represented by the following formulas (a₂) to (h₂):



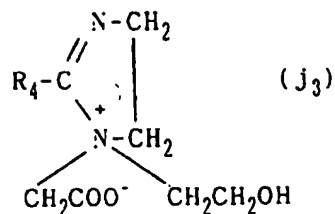
wherein R_1 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms; R_2 and R_3 may be the same or different from each other and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms; HA

represents an inorganic or organic acid; AO represents an oxyalkylene group having 2 to 4 carbon atoms; l and m are each such an integer that l plus m would be a numerical value of above zero and 300 or below; and W_1 , W_2 , W_3 and W_4 may be the same or different from one another and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms.

The present invention includes, further, a deinking method comprising at least a step of liberating ink from waste paper as a raw material and a step of removing the liberated ink therefrom by flotation, characterized in that one or two or more deinking agent(s) selected from among the above nonionic surfactants (A) to (D) is(are) used; the pH in the system during flotation is controlled to 4 to 9; and an amphoteric compound(s) is(are) allowed to be present in the system during flotation. In this case, the amphoteric compound(s) is(are) preferably one or more compounds selected from the group consisting of those represented by the following formulas (a₃) to (j₃), phospholipids (k₃) and proteins (l₃):



and



wherein R_1 , R_2 and R_3 may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms; R_4 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms; M represents a hydrogen

atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an ammonium group; Y_1 represents a group represented by the formula: $R_5NHCH_2CH_2-$ (wherein R_5 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms); Y_2 represents a hydrogen atom or a group represented by the formula: $R_5NHCH_2CH_2-$ (wherein R_5 is as defined above); Z_1 represents a group represented by the formula: $-CH_2COOM$ (wherein M is as defined above); and Z_2 represents a hydrogen atom or a group represented by the formula: $-CH_2COOM$ (wherein M is as defined above).

As described above, increase of lathering during flotation is observed in deinking treatment according to the method disclosed in Japanese Patent Publication-A 54-23705. As a result of investigations made by the present inventors, it is confirmed that the above phenomenon is caused by using a nonionic or anionic polyelectrolyte such as polyacrylamide (PAM) under such a condition that the aluminum ion concentration of the system is high in flotation. In contrast, the deinking method of the present invention, wherein a nonionic surfactant is employed as a deinking agent, and the flotation is effected at a pH of from 4 to 9 in the presence of a cationic

compound, an amine, an acid salt of an amine or an amphoteric compound, provides such a marked effect that deinked pulp having a high quality can be obtained at a high recovery. It is considered that the above effect can be attained by the present invention because ink is sufficiently liberated from fibers of waste paper by the use of a nonionic surfactant, and the liberated ink is efficiently collected for the removal thereof because of the presence of a cationic compound, an amine, an acid salt of an amine or an amphoteric compound at a pH falling within a range of from 4 to 9 in flotation.

Further scope and applicability of the present invention will become apparent from the detailed description and examples given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description and these examples.

Detailed Description of the Invention

The deinking method of the present invention comprises at least steps of liberating ink from waste

paper and removing the liberated ink from a flotation system.

Next, the nonionic surfactants to be used as deinking agents in the present invention will now be illustrated.

Nonionic surfactant (A): A reaction product obtained by adding an alkylene oxide to a mixture of an oil & fat and an alcohol

Nonionic surfactant (A) is an alkylene oxide adduct of a mixture of an oil & fat and a mono- or polyhydric alcohol. The alkylene oxide is added to the mixture described above in an amount, on the average, of 5 to 300 moles, preferably 20 to 150 moles, per mole of the mixture. Examples of the alkylene oxides include ethylene oxide, propylene oxide and butylene oxide, and they may be used singly or in the form of a mixture of two or more of them.

The mixing ratio of the oil & fat to the alcohol is preferably 1/0.1 to 1/6, particularly preferably 1/0.3 to 1/3 by mole. When this ratio falls within the range described above, a reclaimed pulp having an excellent appearance can be obtained since the liberation of ink is efficiently attained.

Examples of the oils & fats as a raw material of nonionic surfactant (A) include vegetable oils such as

coconut oil, palm oil, olive oil, soybean oil, rape seed oil and linseed oil, animal oils such as lard, beef tallow and bone oil, and fish oils; hardened oils thereof and semi-hardened oils thereof; and recovered oils obtained in refining processes of these oils & fats.

Examples of the monohydric alcohols as a raw material of nonionic surfactant (A) include those having an alkyl or alkenyl moiety of 8 to 24 carbon atoms and those having an alkylphenyl moiety wherein the alkyl moiety has 6 to 14 carbon atoms. Specific examples thereof include 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, 1-pentadecanol, 1-hexadecanol, 1-heptadecanol, 1-octadecanol, 1-nonadecanol, 1-eicosanol, 1-heneicosanol, 1-docosanol, 1-tricosanol, 1-tetracosanol, 2-octanol, 2-nonanol, 2-decanol, 2-undecanol, 2-dodecanol, 2-tridecanol, 2-tetradecanol, 2-pentadecanol, 2-hexadecanol, 2-heptadecanol, 2-octadecanol, 2-nonadecanol, 2-eicosanol, 2-octen-1-ol, 2-dodecen-1-ol, 2-undecen-1-ol, 2-tetradecen-1-ol, 2-pentadecen-1-ol, 2-hexadecen-1-ol, 2-octadecen-1-ol, 8-nonen-1-ol, 10-undecen-1-ol, 11-dodecen-1-ol, 12-tridecen-1-ol, 15-hexadecen-1-ol, oleyl alcohol, elaidyl alcohol, linoleyl alcohol, linolenyl alcohol.

eleostearyl alcohol, ricinoyl alcohol, cyclononanol, cyclodecanol, cycloundecanol, cyclododecanol, cyclotridecanol, cyclotetradecanol, cyclopentadecanol, cyclohexadecanol, cycloheptadecanol, cyclooctadecanol, cyclononadecanol, cycloeicosanol, octylphenol and nonylphenol.

Examples of the polyhydric alcohols as a raw material of nonionic surfactant (A) include ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, 1,6-hexanediol, 2-ethylbutane-1,2,3-triol, glycerol, trimethylolpropane, trimethylol-ethane, 1,2,4-butanetriol, 1,2,6-hexanetriol, 1,1,1-trimethylolhexane, tetramethylolcyclohexanols, diglycerol, mannitane, pentaerythritol, erythritol, arabitol, sorbitol, D-glycero-D-galactoheptose, D-glycero-D-glucoheptose, D-glycero-D-mannoheptose, D-glycero-L-mannoheptose, D-altroheptulose, D-mannoheptulose, D-altro-3-heptulose, D-glycero-D-galaheptitol, D-erythro-D-galaoctitol, D-glycero-D-manno-octulose, D-erythro-L-gulonulose, cellobiose, maltose, lactose, gentianose, cellotriose and stachyose.

Nonionic surfactant (B): A compound represented by the formula: $\text{RCOO}(\text{AO})_n\text{R}'$ (wherein R represents an alkyl or alkenyl group having 7 to 23 carbon atoms; R'

represents a hydrogen atom, an alkyl group having 1 to 22 carbon atoms, an alkenyl group having 2 to 22 carbon atoms, or an acyl group having 2 to 22 carbon atoms; AO represents an oxyalkylene group having 2 to 4 carbon atoms; and m is an integer of 1 or more)

When the carbon atom number of the alkyl or alkenyl group in the definition of R is 7 to 23, nonionic surfactant (B) exhibits an excellent ink-collecting ability and an excellent ink-liberating ability to thereby provide reclaimed pulp having a high whiteness and an excellent appearance.

When the carbon atom number of the alkyl, alkenyl or acyl group in the definition of R' is 22 or less, or R' represents a hydrogen atom, nonionic surfactant (B) exhibits an excellent ability for liberating ink from cellulose to thereby provide reclaimed pulp having an excellent appearance, and exhibits an appropriate lathering power to thereby attain an excellent workability.

Nonionic surfactant (B) is produced by adding an alkylene oxide to a fatty acid by a conventional method, optionally followed by esterification or acylation. The alkylene oxide is added to a fatty acid in an amount, on the average, of 5 to 300 moles, preferably 10 to 150 moles, per mole of the fatty

acid. That is, nonionic surfactant (B) is generally a reaction product mixture comprising compounds each represented by the above formula: $\text{RCOO}(\text{AO})_n\text{R}'$. Examples of the alkylene oxides include those described in the above explanation relating to nonionic surfactant (A). It is preferred to use ethylene oxide and propylene oxide in a molar ratio of ethylene oxide to propylene oxide of 1/5 to 5/1 in the production of nonionic surfactant (B).

Examples of the fatty acids to be used for producing nonionic surfactant (B) include those having an alkyl or alkenyl moiety, corresponding to R, of 7 to 23 carbon atoms, and specific examples thereof include caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, oleic acid, elaidic acid, linoleic acid, linolenic acid, stearolic acid, ricinolic acid, ricinoelaidic acid, nonadecanoic acid, arachidic acid, heneicosanoic acid, behenic acid, brassidic acid, erucic acid, tricosanoic acid, tetracosanoic acid, coconut oil fatty acid, beef tallow fatty acid, palm oil fatty acid, tall oil fatty acid, rape oil fatty acid and fish oil fatty acid. Among nonionic surfactants (B), those having an alkyl

or alkenyl group represented by R of 11 to 23 carbon atoms are preferred.

Nonionic surfactant (C): A compound represented by the formula: $RO(AO)_nH$ (wherein R represents an alkyl or alkenyl group having 8 to 24 carbon atoms; AO represents an oxyalkylene group having 2 to 4 carbon atoms; and n is an integer of 1 or more)

When the carbon atom number of the alkyl or alkenyl group in the definition of R is 8 to 24, nonionic surfactant (C) exhibits an excellent ability for liberating ink from cellulose to thereby provide reclaimed pulp having a high whiteness and an excellent appearance.

Nonionic surfactant (C) is produced by adding an alkylene oxide to a monohydric alcohol by a conventional method. The alkylene oxide is added to a monohydric alcohol in an amount, on the average, of 5 to 300 moles, preferably 7 to 150 moles, per mole of the monohydric alcohol. That is, nonionic surfactant (C) is generally a reaction product mixture comprising compounds each represented by the above formula: $RO(AO)_nH$. Examples of the alkylene oxides include those described in the above explanation relating to nonionic surfactant (A). It is preferred to use ethylene oxide and propylene oxide in a molar ratio of

ethylene oxide to propylene oxide of 1/5 to 5/1 in the production of nonionic surfactant (C).

Examples of the monohydric alcohols to be used for producing nonionic surfactant (C) include those having an alkyl or alkenyl moiety of 8 to 24 carbon atoms and those having an alkylphenyl moiety wherein the alkyl moiety has 6 to 14 carbon atoms, and specific examples thereof include those described in the above explanation relating to nonionic surfactant (A). Among nonionic surfactants (C), those having an alkyl or alkenyl group represented by R of 14 to 24 carbon atoms are preferred.

Nonionic surfactant (D): A reaction product obtained by adding an alkylene oxide to a polyvalent carboxylic acid or an acid anhydride thereof; or a reaction product obtained by adding an alkylene oxide to a mixture of a polyvalent carboxylic acid or an acid anhydride thereof, and alcohol

Examples of the polyvalent (or polybasic) carboxylic acids and acid anhydride thereof as a raw material of nonionic surfactant (D) include oxalic acid, malonic acid, succinic acid, methylsuccinic acid, maleic acid, glutaric acid, adipic acid, phthalic acid, fumaric acid, itaconic acid, malic acid, tartaric acid, maleated oleic acid, citric acid,

percitric acid, trimellitic acid, butane-tetracarboxylic acid, pyromellitic acid, tetradecane-hexacarboxylic acid, maleic anhydride, succinic anhydride, oxalic anhydride, itaconic anhydride, glutaric anhydride, phthalic anhydride, trimellitic anhydride, pyromellitic anhydride and stearylsuccinic anhydride.

Further, dimer acids and polymer acids of higher fatty acids having 14 to 22 carbon atoms are included in the scope of the polyvalent carboxylic acid. Dimer acids and polymer acids herein can be synthesized by a method wherein a monoolefinic carboxylic acid or a diolefinic carboxylic acid, such as an unsaturated fatty acid monomer, e.g., oleic acid, linoleic acid or linolenic acid, is subjected to thermal polymerization such as a Diels-Alder reaction, or another method. The polymer acid herein is a polycarboxylic acid having three or more carboxyl groups in a molecule and does not includes a dimer acid. The dimer acid or polymer acid used herein may be a mixture thereof with an unreacted monomer acid. That is, it is not concerned that an unreacted monomer acid is present as far as the effects of the present invention are not failed.

Examples of the alcohols as a raw material of

nonionic surfactant (D) include monohydric alcohols and polyhydric alcohols, and specific examples thereof include those described in the above explanation relating to nonionic surfactant (A).

In the production of nonionic surfactant (D) with a polyvalent carboxylic acid or an acid anhydride thereof (I) and an alcohol (II), the compounds (I) and (II) are preferably used in a molar ratio of (I) to (II) of 1/0.02 to 5/1, particularly 1/0.1 to 3/1. When the molar ratio falls within this range, the above-mentioned nonionic surfactant (D) can efficiently collect fine ink drops and the collected ink drops are effectively removed out from the system in flotation. Therefore, a reclaimed pulp having a high whiteness is provided.

The nonionic surfactant may be added in any step of the deinking process. However, it is usually added in a pulping step. The addition amount thereof is not specifically restricted. A sufficient ink-liberating effect is not achieved with only a deinking agent other than these nonionic surfactants of the present invention. A known deinking agent other than nonionic surfactants (A) to (D) described above may be used in combination therewith.

The flotation method as one of deinking methods

is characterized in that a pulp/water slurry is lathered by a suitable means such as a physical means and a chemical means, ink drops adhere to floated foams and the resulting foams with ink drops are rejected to thereby separate ink from pulp. In the deinking method of the present invention, at least part of the flotation step is effected at a pH in a range of from 4 to 9, preferably from 6 to 8. Therefore, the pH of the pulp/water slurry may be adjusted at a pH in a range of from pH4 to pH9 in any step before flotation.

The steps prior to flotation are effected generally at a basic pH. Therefore, in the present invention, a suitable acid or an aqueous solution thereof is added to the pulp/water slurry before or during flotation to adjust the pH of the slurry to a value in the above-mentioned range. An acid or an aqueous solution thereof may be added to the water which is poured into the slurry before or during flotation, though the addition method of the acid is not specifically restricted. Examples of the acids to be used for adjusting the pH of the slurry include inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid, salts thereof, and organic acids such as acetic acid, formic acid and citric acid. The

method for adjusting the pH of the slurry is not restricted to those using acids. When the pH of the slurry in at least part of the flotation step is a value within the range described above, an increase in whiteness of the reclaimed pulp, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery are attained. Further, apparatuses and pulp fibers per se are affected by the properties of the slurry.

The deinking method of the present invention is also characterized in that a cationic compound, an amine, an acid salt of an amine or an amphoteric compound is to be present in the system in flotation.

The cationic compound herein is cationic or has a cationic group at pH 4 to 9 in flotation. Examples of the cationic compounds include mono(long-chain)alkyl-type quaternary ammonium salts, di(long-chain)alkyl-type quaternary ammonium salts, pyridinium salts having a substituent at the nitrogen atom thereof, and cationic polymers. In particular, the compounds represented by the above formulas (a₁) to (e₁) and cationic polymers represented by the above formulas (f₁) to (j₁) each of which has a cationic nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000 are preferred.

In the respective formulas (a₁) to (e₁), examples of the groups in the definitions of R₁ and R₂ include lauryl group, myristyl group, cetyl group, stearyl group, behenyl group, oleyl group and linoleyl group. R₁ and R₂ may be the same or different from each other. Examples of the alkyl groups each having 1 to 8 carbon atoms in the definitions of R₃, R₄ and R₅ include methyl group, ethyl group, propyl group, butyl group, hexyl group, octyl group, isopropyl group and isobutyl group. R₃, R₄ and R₅ may be the same or different from one another. Examples of the acyl groups in the definition of Z include those derived from fatty acids each having 2 to 24 carbon atoms, e.g., formyl group, acetyl group, propionyl group, butyryl group, lauroyl group, myristoyl group, palmitoyl group, stearoyl group, isobutyryl group, oleoyl group and methacryl group. Examples of the groups in the definition of R₆ include octyl group, lauryl group, myristyl group, cetyl group, stearyl group, behenyl group, hexacosyl group, hexatriacontyl group, oleyl group and linolenyl group. X⁻ is a counter ion and examples thereof include a hydroxyl ion, halide ions, monoalkylsulfate ions wherein the alkyl portion has 1 to 3 carbon atoms, and anions derived from inorganic and organic acids. Specially, X⁻ represents a halide ion such as a

chloride ion, a bromide ion and a fluoride ion, a monoalkylsulfate ion such as a methylsulfate ion and an ethylsulfate ion, a counter ion derived from an inorganic acid such as sulfuric acid, nitric acid, carbonic acid and phosphoric acid, or another counter ion derived from a mono- or polyvalent organic acid such as acetic acid and citric acid.

The cationic polymers represented by the above formulas (f₁) to (j₁) each has a weight-average molecular weight of 2,000 to 3,000,000, preferably 10,000 to 1,000,000 and contains 0.01 to 35 % by weight, preferably 0.01 to 10 % by weight, still more preferably 0.1 to 5 % by weight, of cationic nitrogen atoms. The cationic nitrogen content is determined, for example, by determining the nitrogen content (%) of the polymer by Kjeldahl method and multiplying the nitrogen content (%) determined by the ratio of the cationic nitrogen to the total nitrogen which is calculated from the molecular formula of the polymer.

Examples of the above-mentioned cationic polymers include polymers comprising acrylamide and modified with a group having a quaternary ammonium group, such as acrylamide polymers modified with a group having a quaternary ammonium group and copolymers of acrylamide with an acrylate modified with a group having a

quaternary ammonium group; polymers comprising an acrylate and modified with a group having a quaternary ammonium group, such as acrylate polymers modified with a group having a quaternary ammonium group and copolymers of an acrylate with the other acrylate modified with a group having a quaternary ammonium group; styrene polymers modified with a group having a quaternary ammonium group; diallylamine polymers modified with a group having a quaternary ammonium group; cationized cellulose; and cationed chitosan.

In the respective formulas (f₁) to (j₁), examples of the groups in the definitions of R₁, R₂, R₃, R₆, R₇, R₈ and R₉ include methyl group, ethyl group, propyl group, butyl group, hexyl group, octyl group, lauryl group, myristyl group, cetyl group, stearyl group, behenyl group, oleyl group, linoleyl group, isopropyl group and isobutyl group. X⁻ and W⁻ in the above formulas (f₁) to (j₁) are each a counter ion and examples thereof include those described in the above explanation relating to X⁻ in formulas (a₁) to (e₁). Further, the A0 in the above formulas (f₁) to (j₁) refers to an oxyalkylene group having 2 to 4 carbon atoms, and examples thereof include oxyethylene group, oxypropylene group and oxybutylene group.

The amine or the acid salt of the amine herein

has a nitrogen atom which may be cationized at pH 4 to 9 in flotation. Examples of the amines and the acid salts of amines include primary amines, secondary amines, tertiary amines, cyclic amines, imidazoles and imidazolines; inorganic acid salts of these amines; organic acid salts of these amines; and polymers having an amino group. In particular, the compounds represented by the above formulas (a₂) to (h₂) and polymers represented by the above formulas (i₂) to (l₂) each of which has an amino-nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000 are preferred.

In the respective formulas (a₂) to (h₂), examples of the groups in the definition of R₁ include those described in the above explanation relating to R₆ in formulas (a₁) to (e₁). Examples of the groups in the definitions of R₂ and R₃ include those described in the above explanation relating to R₁, R₂, R₃, R₆, R₇, R₈ and R₉ in formulas (f₁) to (j₁). R₂ and R₃ may be the same or different from each other. HA represents an inorganic acid, e.g., hydrochloric acid, sulfuric acid, nitric acid, carbonic acid, phosphoric acid or hydrobromic acid; or a mono- or polyvalent organic acid, e.g., formic acid, acetic acid, propionic acid, butyric acid, lauric acid, stearic acid, malonic acid,

succinic acid, acrylic acid, maleic acid, fumaric acid or citric acid. l and m are each zero or a positive integer with the proviso that l plus m is an integer of 1 to 300. Examples of the alkyl groups in the definitions of W_1 , W_2 , W_3 and W_4 include methyl group, ethyl group, propyl group, butyl group, hexyl group, octyl group, lauryl group, myristyl group, cetyl group, stearyl group, behenyl group, isopropyl group and isobutyl group. W_1 , W_2 , W_3 and W_4 may be the same or different from one another.

Among amines and acid salts of amines represented by the above formulas (a₂) to (h₂), preferred are those represented by the formulas (a₂) to (h₂) wherein R_1 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms; R_2 and R_3 may be the same or different from each other and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms; HA represents an inorganic or organic acid; AO represents an oxyalkylene group having 2 to 4 carbon atoms; l and m are each such an integer that l plus m would be a numerical value of above zero and 300 or below; and W_1 , W_2 , W_3 and W_4 may be the same or different from one another and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms.

The polymers represented by the above formulas (1₁) to (1₂) each has a weight-average molecular weight of 2,000 to 3,000,000, preferably 10,000 to 1,000,000 and contains 0.01 to 35 % by weight, preferably 0.01 to 10 % by weight, still more preferably 0.1 to 5 % by weight, of amino-nitrogen atoms. The amino-nitrogen content is determined, for example, by determining the nitrogen content (%) of the polymer by Kjeldahl method and multiplying the nitrogen content (%) determined by the ratio of the amino-nitrogen to the total nitrogen which is calculated from the molecular formula of the polymer.

Examples of the above-mentioned polymers include linear polyamines such as polyvinylamine and polyethyleneimine; polymers of cyclic amines such as polyvinylpyridine, polyaminostyrene and polyvinylimidazole; formaldehyde condensates such as melamine/formaldehyde condensate and urea/formaldehyde condensate; polymers comprising acrylamide and modified with a group having an amino group, such as acrylamide polymers modified with a group having an amino group and copolymers of acrylamide with an acrylate modified with a group having an amino group; polymers comprising an acrylate and modified with a group having an amino group, such as acrylate polymers

modified with a group having an amino group and copolymers of an acrylate with the other acrylate modified with a group having an amino group; and polymeric amine compounds such as chitosan; and acid salts of these polymers.

In the respective formulas (i₂) to (l₂), examples of the alkyl groups and alkenyl groups in the definitions of R₁, R₂, R₃ and R₆ include methyl group, ethyl group, propyl group, butyl group, hexyl group, octyl group, lauryl group, myristyl group, cetyl group, stearyl group, behenyl group, oleyl group, linoleyl group, isopropyl group and isobutyl group. HA represents an inorganic or organic acid, and examples thereof include those described in the above explanation relating to HA in formulas (a₂) to (h₂).

The amphoteric compound herein has a cationic group at pH 4 to 9 in flotation. Examples of the amphoteric compounds include betaines, amine oxides, phospholipids, proteins and amphoteric polymers. In particular, the compounds represented by the above formulas (a₃) to (j₃), phospholipids (k₃), proteins (l₃) and amphoteric polymers represented by the above formulas (m₃) and (n₃) each of which has a cationic nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000

are preferred. Further, proteins (l_3) each having a weight-average molecular weight of 2,000 to 3,000,000, desirably 10,000 to 1,000,000 and containing 0.01 to 35 % by weight, desirably 0.01 to 10 % by weight, still more desirably 0.1 to 5 % by weight, of cationic nitrogen atoms, are still more preferred.

In the respective formulas (a_3) to (j_3), examples of the alkyl groups and alkenyl groups in the definitions of R_1 , R_2 and R_3 include those described in the above explanation relating to R_1 , R_2 , R_3 and R_6 in formulas (i_2) to (l_2). Examples of the groups in the definitions of R_4 include those described in the above explanation relating to R_6 in formulas (a_1) to (e_1). Examples of the groups in the definitions of R_5 include methyl group, ethyl group, propyl group, butyl group, hexyl group, octyl group, isopropyl group, isobutyl group, lauryl group, myristyl group, cetyl group, stearyl group, behenyl group, hexacosyl group, hexatriacontyl group, oleyl group and linoleyl group.

Examples of the phospholipids (k_3) include phosphatidyl choline, phosphatidyl ethanolamine, sphingomyelin, phosphatidyl serine and lysolecithine. Further, examples of the proteins (l_3) include natural proteins derived from natural materials, e.g., soybean protein or lactoprotein, those prepared by the partial

hydrolysis of the natural proteins, and denatured products of the natural proteins. The molecular weight, kind of the atoms constituting the protein, the degree of the denaturation or the like is not restricted.

Among amphoteric compounds represented by the above formulas (a₃) to (j₃), phospholipids (k₃) and proteins (l₃), preferred are phospholipids (k₃), proteins (l₃) and those represented by the formulas (a₃) to (j₃) wherein R₁, R₂ and R₃ may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms; R₄ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; M represents a hydrogen atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an ammonium group; Y₁ represents a group represented by the formula: R₅NHCH₂CH₂- (wherein R₅ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms); Y₂ represents a hydrogen atom or a group represented by the formula: R₅NHCH₂CH₂- (wherein R₅ is as defined above); Z₁ represents a group represented by the formula: -CH₂COOM (wherein M is as defined above); and Z₂ represents a hydrogen atom or a group represented by the formula: -CH₂COOM (wherein M is as defined above).

The amphoteric polymers other than proteins, and represented by the above formulas (m_3) and (n_3) each has a weight-average molecular weight of 2,000 to 3,000,000, preferably 10,000 to 1,000,000 and contains 0.01 to 35 % by weight, preferably 0.01 to 10 % by weight, still more preferably 0.1 to 5 % by weight, of cationic nitrogen atoms. The cationic nitrogen content is determined, for example, by determining the nitrogen content (%) of the polymer by Kjeldahl method and multiplying the nitrogen content (%) determined by the ratio of the cationic nitrogen to the total nitrogen which is calculated from the molecular formula of the polymer.

Examples of the above-mentioned amphoteric polymers include polyvinylbetaines, copolymers of acrylic acid with acrylamide partially modified by Mannich reaction, and copolymers of an dialkylamino-alkyl acrylate with a sulfonated styrene.

In the respective formulas (m_3) and (n_3), examples of the alkyl groups and alkenyl groups in the definitions of R_1 , R_2 and R_3 include those described in the above explanation relating to R_1 , R_2 , R_3 , R_6 , R_7 , R_8 and R_9 in formulas (f_1) to (j_1). R_1 , R_2 and R_3 may be the same or different from one another.

At least one member selected from the group

consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds is used in an amount of 0.001 to 5.0% by weight, preferably 0.01 to 1.0% by weight, based on the weight of waste paper (i.e., the absolute dry weight of waste paper) in flotation. When the above-mentioned at least one member selected is present in the system, i.e., in the slurry, in flotation in such an amount as described above, ink can be selectively removed from the system.

In the present invention, it is necessary that a pulp/water slurry in at least one step of flotation contains the cationic compound, amine, acid salt of amine or amphoteric compound. Therefore, the cationic compound, amine, acid salt of amine or amphoteric compound may be added at any of the steps of the deinking process, as long as the step is not one to be effected after flotation. It may be added in a step before flotation, for example, a disintegration step or a bleaching step, or alternatively added just before flotation or during flotation (e.g., in an early stage of the flotation step). Preferably, the cationic compound, amine, acid salt of amine or amphoteric compound is added to the slurry just before flotation or during flotation, and after adjusting the pH of the slurry to a value in a range of from 4 to 9.

In this case, the cationic compound, amine, acid salt of amine or amphoteric compound is preferably used in such an amount that the pH of the system for flotation is scarcely altered by the addition thereof. "The pH of the system for flotation is scarcely altered" refers that the alteration of the pH of the system is not recognized or recognized only in two places of decimals in the determination of pH. The amount of the cationic compound, amine, acid salt of amine or amphoteric compound that the pH of the flotation system is scarcely altered by the addition thereof is, e.g., from 0.01 to 1.0% by weight based on the weight (i.e., the absolute dry weight) of waste paper.

The flotation step may comprise two or more steps when, for example, the flotation system is circulated. In such a case, the pH of the system has to be regulated to a value in a range of from 4 to 9 at least one flotation step. It is preferred that the pH of the system in the step, among steps of flotation, immediately before the washing step is regulated as described above. At least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds also has to be present in the system having a pH of from 4 to 9 in at least one step of flotation.

In the deinking method of the present invention, the calcium ion concentration of the system, i.e., the slurry, in flotation is not specifically restricted. In order to obtain a reclaimed pulp having a higher quality, however, the calcium ion concentration of the system in flotation is preferably controlled to a value in the range of from 10 to 400 ppm, particularly from 100 to 250 ppm. When the calcium ion concentration falls within the above-mentioned range, fine drops of ink can be selectively flocculated one another to give ink drops having an optimum size for flotation reject. Therefore, ink is easily rejected by flotation to give a reclaimed pulp having a higher whiteness and a less residual ink spots.

For the regulation of the calcium ion concentration of the system, inorganic calcium salts such as calcium chloride and calcium carbonate, and minerals such as lime can be used. Further, an animal bone, a shell or the like may be used as the source of the calcium ion. In such a case, the animal bone or the like is reacted with an acid to thereby ionize. Although the calcium ion concentration of the system in flotation is preferably regulated to a value in the above-mentioned range, the calcium ion concentration of the system in any step other than the flotation

step is not restricted. Therefore, the calcium ion concentration of the system may be adjusted in any step (such as the pulping step) prior to the flotation step, as far as the liberation of ink is not affected.

In the deinking method of the present invention, the aluminum ion concentration of the system in flotation is desirably regulated to 40 ppm or less, particularly 25 ppm or less. For the regulation of the aluminum ion concentration of the system, it is preferred to take the kind and amount of water used in flotation into consideration. For example, white water resulting from paper-making and/or city water are used in a suitable amount. When the aluminum ion concentration of the system in flotation is regulated as described above, not only both an improvement in the whiteness of the reclaimed pulp and a decrease of the residual ink spots of the reclaimed paper are achieved, but also the recovery of pulp is enhanced. Although the aluminum ion concentration of the system in flotation is preferably regulated to a value in the above-mentioned range, the aluminum ion concentration of the system in any step other than the flotation step is not restricted. Therefore, the aluminum ion concentration of the system may be adjusted in any step (such as the pulping step) prior to the flotation

step, as far as the liberation of ink is not affected.

The deinking method of the present invention described above is characterized in that at least one of nonionic surfactants (A) to (D) is used, and that at least part of the flotation step is effected in the presence of at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds at a pH in a range of from 4 to 9; and comprises at least steps of liberating ink from waste paper and removing the liberated ink from a flotation system. Other steps can be carried out according to the conventional deinking method. That is, the deinking method may comprise, as the main steps, a disintegrating (or pulping) step, an aging step, (a kneading step, if necessary), a flotation step and a washing step. The deinking method may further comprise other step(s), if necessary. The respective steps may be carried out two or more times.

According to the present invention, deinked pulp having a higher whiteness and a less residual ink spots can be obtained from waste paper as the raw material. Therefore, it becomes possible to reduce the production cost of the deinked pulp since bleaching chemicals such as caustic soda, sodium

silicate, hydrogen peroxide and chelating agents are necessitated in only small amounts and the recovery of pulp is increased.

Although the mechanism why the deinking method of the present invention exhibits such an excellent deinking effect is not necessarily clarified, it is considered as follows:

That is, ink is sufficiently liberated from pulp by using a nonionic surfactant as the deinking agent and, further, the reduction of the pH of the system before or during flotation brings about an alteration in conditions of the interface between pulp and ink to cause existing a cationic compound, an amine, an acid salt of an amine or an amphoteric compound to adsorb preferentially on the ink, thereby aggregating ink by the cohesion of the cationic compounds (amines, acid salts of amines or amphoteric compounds) therebetween at their hydrophobic portions. In this case, the presence of the nonionic surfactant in the system prevents the re-adhesion of ink to pulp. When the nonionic surfactant is not present in the system, the cationic compound or the like adsorbs on both ink and pulp, which results in causing the re-adhesion of ink to the pulp.

In any event, there are essentials in the

deinking method of the present invention that (1) a nonionic surfactant is used as a deinking agent, (2) the pH of the system is regulated to a low value in the presence of the above nonionic surfactant, and (3) aggregation of ink is carried out with a cationic compound, an amine, an acid salt of an amine or an amphoteric compound.

Examples

The present invention will be described in detail with reference to the following Examples which should not be considered to limit the present invention.

<Cationic compounds>

The cationic compounds used in the following Examples I-1 to I-10 will be shown in the following Tables I-1 to I-5.

In Tables I-1 to I-5, each numeral in the columns of R_1 to R_6 , R_{6a} and R_{6b} means the carbon atom number of a linear alkyl group as a substituent; and "18 Fl", "18 Hyd" and "12 Hyd" refer oleyl group, β -hydroxystearyl group and β -hydroxylauryl group, respectively.

Further, in the following Examples, "EO" and "PO" refer oxyethylene group and oxypropylene group, respectively; and the subscript refers an average molar number of ethylene oxide or propylene oxide added.

Table I-1

General formula	Compd. No.	Substituent and counter ion				
		R ₁	R ₂	R ₃	R ₄	X ⁻
$\left(\begin{array}{c} R_1 \quad R_3 \\ \diagdown \quad / \\ N \\ / \quad \diagdown \\ R_2 \quad R_4 \end{array} \right)^+ X^-$	a ₁ -1	10	24	1	1	Cl ⁻
	a ₁ -2	12	12	1	2	Br ⁻
	a ₁ -3	12	18	1	1	CH ₃ COO ⁻
	a ₁ -4	12	12	8	8	1/2 SO ₄ ²⁻
	a ₁ -5	18	18	2	2	Cl ⁻
	a ₁ -6	18	18	4	4	Cl ⁻
	a ₁ -7	18	18 Hyd	2	2	Cl ⁻
	a ₁ -8	18 F1	18 F1	2	2	Cl ⁻

Table I-2

General formula	Compd. No.	Substituent and counter ion				
		R ₃	R ₄	R ₅	R ₆	X ⁻
$\left(\begin{array}{c} R_6 \quad R_4 \\ \diagdown \quad / \\ N \\ / \quad \diagdown \\ R_3 \quad R_5 \end{array} \right)^+ X^-$	b ₁ - 1	1	1	1	12	Cl ⁻
	b ₁ - 2	1	1	8	12	Br ⁻
	b ₁ - 3	1	1	1	18	CH ₃ COO ⁻
	b ₁ - 4	4	4	4	18	1/2 SO ₄ ²⁻
	b ₁ - 5	1	1	benzyl	18	Cl ⁻
	b ₁ - 6	2	2	2	22	Cl ⁻
	b ₁ - 7	1	1	1	34	Cl ⁻
	b ₁ - 8	1	1	1	12 Hyd	Cl ⁻
	b ₁ - 9	1	1	1	18 Fl	Cl ⁻
	b ₁ -10	1	1	(EO) ₅₀ -H	18	Cl ⁻
	b ₁ -11	1	(EO) ₂₀ -H	(EO) ₂₀ -H	18	Cl ⁻
	b ₁ -12	(EO) ₂₀ -H	(EO) ₂₀ -H	(EO) ₂₀ -H	18	Cl ⁻

Table I-3

General formula	Compound No.	Substituent and counter ion	
		Y	X ⁻
$Y - N^+ \text{ (benzene ring) } X^-$	c ₁ -1	C ₈ H ₁₇ COOCH ₂	Cl ⁻
	c ₁ -2	C ₁₂ H ₂₅ CONHCH ₂	Cl ⁻
	c ₁ -3	C ₁₈ H ₃₇ OCH ₂	Br ⁻
	c ₁ -4	C ₁₂ H ₂₅	Br ⁻

Table I-4

General formula	Compound No.	Substituent and counter ion		
		R ₃	R ₆	X ⁻
$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \diagup \\ \text{R}_6\text{COOCH}_2\text{CH}_2\text{N}^+ \\ \\ \text{R}_3 \quad \text{CH}_2\text{CH}_2\text{OH} \end{array} \quad \text{X}^-$	d ₁ -1	1	12	Cl ⁻
	d ₁ -2	4	18 F1	Cl ⁻
	d ₁ -3	8	22	Br ⁻

Table I-5

General formula	Compound No.	Substituent and counter ion		
		R _{6a}	R _{6b}	X ⁻
$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \diagup \\ \text{R}_{6b}\text{-O-CH}_2\text{CH}_2\text{N}^+ \\ \\ \text{R}_{6a} \quad \text{CH}_2\text{CH}_2\text{OH} \end{array} \quad \text{X}^-$	e ₁ -1	12	12	Cl ⁻
	e ₁ -2	18	18 F1	Cl ⁻
	e ₁ -3	12	22	Br ⁻

Example I-1

Waste papers (news papers/leaflets = 75/25) recovered in a city were cut into pieces (2 x 5 cm). A given amount thereof was fed into a bench disintegrator. Then, warm water, 1% by weight (based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide and 0.2% by

weight (based on the waste papers) of an $\text{EO}_{10}/\text{PO}_{10}$ block adduct of stearyl alcohol as a deinking agent were added thereto to prepare a mixture. The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 5% by weight. The resulting pulp slurry was maintained at 40°C for 60 minutes, and then warm water was added to the pulp slurry. Thus, a pulp slurry having a pulp concentration of 1% by weight was prepared. Hydrochloric acid was added to the pulp slurry to adjust the pH thereof to a value shown in Table I-6. To the pulp slurry, a cationic compound shown in Table I-1 or I-2, and Table I-6 was further added in an amount shown in Table I-6. By the addition of the cationic compound, the pH of the resulting pulp slurry was scarcely altered. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation).

The whitenesses of the pulp sheet prepared from the pulp slurry (before flotation) and the pulp slurry (after flotation) were measured. The residual ink area ratio of the pulp sheet obtained from the pulp slurry (after flotation) was also measured.

Specially, aluminum sulfate was added to each of the pulp slurry (before flotation) and the pulp slurry (after flotation) to adjust the pH thereof to 5, and the resulting pulp slurries were each treated on a TAPPI standard sheet machine to give pulp sheet. The pulp sheet thus obtained were dried under airing. The whitenesses of the resulting pulp sheet were determined with a color-difference meter, and the residual ink area ratio of the pulp sheet obtained from the pulp slurry (after flotation) was determined with an image analyzer (magnification: x100).

An increase by 1% in the whiteness of the pulp sheet and a reduction by 0.1% in the residual ink area ratio thereof can be recognized with naked eyes such that the quality of the pulp sheet was sufficiently improved.

The recovery of pulp in flotation was determined from the absolute dry weight of the pulp contained in the pulp slurry before flotation and the absolute dry weight of the pulp contained in flotation reject [i.e., [(the absolute dry weight of the pulp contained in the pulp slurry before flotation) - (the absolute dry weight of the pulp contained in flotation reject)] x 100 / (the absolute dry weight of the pulp contained in the pulp slurry before flotation)]. The results

thereof are shown in Table I-6.

Table I-6

Test No.	Cationic compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
1	None	-	10.0	45.0	52.2	0.752	86.8
2	None	-	9.0	45.4	52.8	0.683	87.2
3	None	-	8.0	44.9	53.3	0.411	88.3
4	None	-	7.0	45.6	53.6	0.365	88.9
5	None	-	6.0	45.0	54.0	0.329	88.9
6	None	-	5.0	44.6	53.1	0.431	89.1
7	None	-	4.0	44.3	52.9	0.625	87.6
8	a ₁ -4	0.10	9.0	45.0	55.7	0.252	89.2
9	a ₁ -4	0.10	8.0	44.8	57.4	0.151	89.0
10	a ₁ -4	0.10	7.0	44.6	57.2	0.149	93.1
11	a ₁ -4	0.10	6.0	44.7	56.8	0.179	92.5
12	a ₁ -4	0.10	5.0	44.3	56.6	0.221	92.7
13	a ₁ -4	0.10	4.0	44.3	56.0	0.239	91.3
14	b ₁ -1	0.06	9.0	45.5	55.9	0.247	88.9
15	b ₁ -1	0.06	8.0	45.0	57.7	0.147	88.8
16	b ₁ -1	0.06	7.0	45.1	57.4	0.146	93.0
17	b ₁ -1	0.06	6.0	44.9	57.1	0.167	92.3
18	b ₁ -1	0.06	5.0	44.8	56.9	0.215	92.4
19	b ₁ -1	0.06	4.0	44.2	56.3	0.243	91.3
20	b ₁ -11	0.03	9.0	45.1	55.8	0.242	87.8
21	b ₁ -11	0.03	8.0	45.0	58.0	0.136	87.4
22	b ₁ -11	0.03	7.0	44.7	57.7	0.144	91.3
23	b ₁ -11	0.03	6.0	44.7	57.4	0.150	90.7
24	b ₁ -11	0.03	5.0	44.5	56.8	0.199	91.2
25	b ₁ -11	0.03	4.0	44.3	56.2	0.215	89.9

Note)

The amount of the cationic compound is expressed by % by weight based on the waste papers (i.e., the absolute dry weight of the waste papers). The same will be applied to the following Examples I-2 to I-10.

In the Tests described above, Test No. 1 is effected in a similar manner as that of a conventional industrial deinking method. According to the methods of Test Nos. 8 to 25 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound at a specific pH, as compared with those of Test Nos. 1 to 7 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-2

Deinking test was carried out according to the method described in Example I-1 by using cationic compounds shown in Tables I-1 and I-7. The result are shown in Table I-7.

Table I-7

Test No.	Cationic compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
26	None	-	10.0	45.1	52.3	0.749	86.8
27	None	-	7.0	45.3	54.6	0.431	88.8
28	a ₁ -1	0.10	7.0	45.2	57.4	0.144	92.3
29	a ₁ -2	0.10	7.0	45.0	57.2	0.151	92.2
30	a ₁ -3	0.10	7.0	45.2	57.2	0.148	92.1
31	a ₁ -4	0.10	7.0	44.6	57.2	0.155	93.3
32	a ₁ -5	0.10	7.0	45.2	57.4	0.148	92.7
33	a ₁ -6	0.10	7.0	45.2	57.6	0.147	93.4
34	a ₁ -7	0.10	7.0	45.2	57.4	0.142	92.0
35	a ₁ -8	0.10	7.0	45.1	57.3	0.146	92.7

According to the methods of Test Nos. 28 to 35 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound shown in Table I-1 at a specific pH, as compared with those of Test Nos. 26 and 27 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-3

Deinking test was carried out according to the method described in Example I-1 by using cationic

compounds shown in Tables I-2 and I-8. The results are shown in Table I-8.

Table I-8

Test No.	Cationic compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation	After flotation	
36	None	-	10.0	45.0	52.3	0.744	86.9
37	None	-	7.0	45.2	54.3	0.446	88.8
38	b ₁ - 1	0.10	7.0	45.1	57.2	0.157	91.7
39	b ₁ - 2	0.10	7.0	45.1	57.8	0.143	92.4
40	b ₁ - 3	0.10	7.0	45.0	58.0	0.101	92.6
41	b ₁ - 3	0.10	7.0	44.9	57.3	0.145	92.7
42	b ₁ - 5	0.10	7.0	44.8	57.6	0.143	92.1
43	b ₁ - 6	0.10	7.0	45.0	57.0	0.165	92.8
44	b ₁ - 7	0.10	7.0	45.2	58.0	0.137	93.2
45	b ₁ - 8	0.10	7.0	45.4	57.5	0.148	92.3
46	b ₁ - 9	0.10	7.0	45.3	57.7	0.146	92.9
47	b ₁ -10	0.10	7.0	45.2	57.2	0.151	91.6
48	b ₁ -11	0.10	7.0	45.0	57.6	0.143	91.4
49	b ₁ -12	0.05	7.0	45.0	57.1	0.156	92.3
50	b ₁ -12	0.10	7.0	45.0	57.9	0.135	91.9
51	b ₁ -12	0.20	7.0	45.1	59.2	0.123	91.0

According to the methods of Test Nos. 38 to 51 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound shown in Table I-2 at a specific pH, as compared with those of Test Nos. 36 and 37 (comparative methods), there can be expected to attain

an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-4

Deinking test was carried out according to the method described in Example I-1 by using cationic compounds shown in Tables I-3 and I-9. An EO₂₀ adduct of stearic acid was used as the deinking agent in the present Example. The results are shown in Table I-9.

Table I-9

Test No.	Cationic compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
52	None	-	10.0	45.1	52.0	0.772	86.8
53	None	-	7.0	45.4	54.1	0.465	88.2
54	c ₁ -1	0.05	7.0	45.9	57.3	0.153	92.1
55	c ₁ -2	0.05	7.0	45.2	56.9	0.158	92.0
56	c ₁ -3	0.05	7.0	45.1	57.2	0.155	92.1
57	c ₁ -4	0.05	7.0	45.1	57.6	0.149	91.0

According to the methods of Test Nos. 54 to 57 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound shown in Table I-3 at a specific pH, as compared with those of Test Nos. 52 and 53

(comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-5

Deinking test was carried out according to the method described in Example I-1 by using cationic compounds shown in Tables I-4 and I-10. An EO₆₀ adduct of a mixture (1:1 by mole) of beef tallow and glycerol was used as the deinking agent in the present Example. The results are shown in Table I-10.

Table I-10

Test No.	Cationic compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
58	None	-	10.0	45.0	51.7	0.704	85.7
59	None	-	7.0	45.4	53.8	0.411	86.6
60	d ₁ -1	0.10	7.0	44.9	57.6	0.142	92.2
61	d ₁ -2	0.10	7.0	45.3	57.2	0.147	92.4
62	d ₁ -3	0.10	7.0	45.2	56.9	0.152	92.1

According to the methods of Test Nos. 60 to 62 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic

compound shown in Table I-4 at a specific pH, as compared with those of Test Nos. 58 and 59 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-6

Deinking test was carried out according to the method described in Example I-1 by using cationic compounds shown in Tables I-1, I-2 and I-5, and I-11. The results are shown in Table I-11.

Table I-11

Test No.	Cationic compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
63	None	-	10.0	45.1	52.2	0.759	86.8
64	None	-	7.0	45.3	54.4	0.434	88.3
65	e ₁ -1	0.10	7.0	45.1	57.6	0.145	92.1
66	e ₁ -2	0.10	7.0	45.0	57.4	0.151	92.9
67	e ₁ -3	0.10	7.0	44.9	56.9	0.153	92.8
68	a ₁ -2/e ₁ -1	0.05/0.05	7.0	45.3	57.8	0.142	92.5
69	b ₁ -1/e ₁ -2	0.07/0.03	7.0	45.2	57.7	0.145	92.6

According to the methods of Test Nos. 65 to 69 (the methods of the present invention) wherein the

flotation is effected in the presence of a cationic compound shown in Table I-5 optionally together with a cationic compound shown in Table I-1 or I-2 at a specific pH. as compared with those of Test Nos. 63 and 64 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-7

Waste papers (news papers/leaflets = 75/25) recovered in a city were cut into pieces (2 x 5 cm). A given amount thereof was fed into a disintegrator for a high concentration. Then, warm water, 1% by weight (based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide and a deinking agent of Table I-12 in an amount given in Table I-13 were added thereto to prepare a mixture. The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 15% by weight. Warm water was added to the pulp slurry to prepare a pulp slurry having a pulp concentration of 4% by weight.

The resulting pulp slurry was maintained at 40°C for 60 minutes, and then warm water was added to the pulp slurry. Thus, a pulp slurry having a pulp concentration of 1% by weight was prepared. Sulfuric acid was added to the pulp slurry to adjust the pH thereof to a value shown in Table I-13. To the pulp slurry, a cationic compound shown in Table I-1, I-2 or I-3, and Table I-13 was further added in an amount shown in Table I-13. By the addition of the cationic compound, the pH of the resulting pulp slurry was scarcely altered. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation). The pulp slurries were subjected to paper-making in the same manner as that in Example I-1.

The performances of the pulp sheet thus obtained were evaluated in the same manner as that in Example I-1. The results thereof are shown in Table I-13.

Table I-12

Deinking agent No.	Deinking agent	Amount added (based on waste papers)
A1	an EO ₁₀ /PO ₁₀ random adduct of stearic acid	0.2 %
A2	an EO ₃₀ /PO ₂₅ block adduct of dimer acid	0.3 %
A3	an EO ₇₀ /PO ₂₀ block adduct of a mixture (1:1 by mole) of beef tallow and glycerol	0.3 %
A4	Stearic acid	0.5 %

Table I-13

Test No.	Deinking agent No. (See Table I-12)	Amine and acid salt of amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
		Compd. No.	Amount added (%)		Before flotation	After flotation		
70	A1	None	-	10.0	43.9	51.0	0.841	88.5
71	A2	None	-	10.0	44.0	52.2	0.785	86.5
72	A3	None	-	10.0	44.6	52.1	0.771	86.2
73	A4	None	-	10.0	47.8	53.5	0.415	90.0
74	A1	a ₁ -1	0.10	7.0	44.2	56.3	0.204	92.1
75	A2	a ₁ -2	0.10	7.0	44.5	57.5	0.155	90.7
76	A3	b ₁ -6	0.10	7.0	44.6	57.2	0.163	89.9
77	A4	c ₁ -1	0.05	7.0	47.2	58.6	0.150	93.6

According to the methods of Test Nos. 74 to 77
(the methods of the present invention) wherein various

deinking agents are each used and the flotation is effected in the presence of a cationic compound at a specific pH, as compared with those of Test Nos. 70 to 73 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example I-8

Waste papers (news papers/leaflets = 75/25) recovered in a city were cut into pieces (2 x 5 cm). A given amount thereof was fed into a bench disintegrator. Then, warm water, 1% by weight (based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide and 0.2% by weight (based on the waste papers) of an EO₁₀/PO₁₀ block adduct of stearyl alcohol as a deinking agent were added thereto to prepare a mixture. The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 5% by weight. The resulting pulp slurry was maintained at 40°C for 60 minutes, and then warm water was added to the pulp slurry to give a pulp

slurry having a pulp concentration of 1% by weight and a Ca^{2+} ion concentration given in Table I-14. The Ca^{2+} ion concentration of the warm water had been adjusted with CaCl_2 so as to give the Ca^{2+} ion concentration of the resulting pulp slurry shown in Table I-14. Then, hydrochloric acid was added to the resulting pulp slurry to adjust the pH thereof to a value shown in Table I-14. To the resulting pulp slurry, a cationic compound shown in Table I-1 or I-2, and Table I-14 was further added in an amount shown in Table I-14. By the addition of the cationic compound, the pH of the resulting pulp slurry was scarcely altered. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation). The pulp slurries were subjected to paper-making in the same manner as that in Example I-1.

The performances of the pulp sheet thus obtained were evaluated in the same manner as that in Example I-1. The results thereof are shown in Table I-14.

Table I-14

Test No.	Cationic compound		pH in flotation	Ca ²⁺ ion concentration (ppm)	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
	Compound No.	Amount added (%)			Before flotation	After flotation		
78	None	-	10.0	0	44.8	52.1	0.770	86.4
79	None	-	10.0	50	45.0	52.2	0.752	86.8
80	None	-	10.0	100	45.3	52.5	0.743	87.3
81	None	-	10.0	200	45.2	52.6	0.739	87.3
82	None	-	10.0	400	45.0	52.3	0.765	87.6
83	None	-	10.0	800	44.7	51.8	0.781	87.6
84	b ₁ -1	0.06	7.0	0	44.8	57.2	0.162	93.5
85	b ₁ -1	0.06	7.0	50	45.2	57.5	0.145	93.0
86	b ₁ -1	0.06	7.0	100	45.3	58.4	0.091	92.7
87	b ₁ -1	0.06	7.0	200	45.6	59.0	0.086	93.0
88	b ₁ -1	0.06	7.0	400	45.1	57.5	0.128	93.8
89	b ₁ -1	0.06	7.0	800	45.1	56.4	0.221	94.1
90	a ₁ -4	0.10	7.0	0	44.3	57.0	0.172	93.4
91	a ₁ -4	0.10	7.0	200	45.1	58.8	0.092	93.0
92	a ₁ -4	0.10	7.0	800	45.0	56.2	0.229	93.9
93	b ₁ -11	0.03	7.0	0	44.3	57.2	0.161	91.9
94	b ₁ -11	0.03	7.0	200	45.1	59.2	0.085	92.5
95	b ₁ -11	0.03	7.0	800	44.6	56.6	0.219	92.7

Note)

The Ca²⁺ ion concentrations in the above Table were determined in flotation.

According to the methods of Test Nos. 84 to 95 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound at a specific pH at a specific Ca^{2+} ion concentration, as compared with those of Test Nos. 78 to 83 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example I-9

Waste papers (news papers/leaflets = 75/25) recovered in a city were cut into pieces (2 x 5 cm). A given amount thereof was fed into a bench disintegrator. Then, warm water, 1% by weight (based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide and 0.2% by weight (based on the waste papers) of an $\text{EO}_{10}/\text{PO}_{10}$ block adduct of stearyl alcohol as a deinking agent were added thereto to prepare a mixture. The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 5% by weight. The resulting pulp

slurry was maintained at 40°C for 60 minutes, and then warm water was added to the pulp slurry to give a pulp slurry having a pulp concentration of 1% by weight, an Al^{3+} ion concentration given in Table I-15 and a Ca^{2+} ion concentration given in Table I-15. The Al^{3+} ion concentration of the warm water had been adjusted with white water resulting from paper-making (with white water and aluminum sulfate in Test Nos. 99, 103 and 107) so as to give the Al^{3+} ion concentration of the resulting pulp slurry shown in Table I-15. The Ca^{2+} ion concentration of the warm water had been adjusted with CaCl_2 so as to give the Ca^{2+} ion concentration of the resulting pulp slurry shown in Table I-15. Then, hydrochloric acid or sodium hydroxide was added to the resulting pulp slurry to adjust the pH thereof to a value shown in Table I-15. To the resulting pulp slurry, a cationic compound shown in Table I-1 or I-2, and Table I-15 was further added in an amount shown in Table I-15. By the addition of the cationic compound, the pH of the resulting pulp slurry was scarcely altered. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation). The pulp slurries were subjected to paper-making in the same

manner as that in Example I-1.

The performances of the pulp sheet thus obtained were evaluated in the same manner as that in Example I-1. The results thereof are shown in Table I-15.

Table I-15

Test No.	Cationic compound		pH in flotation	Al ³⁺ ion conc. (ppm)	Ca ²⁺ ion conc. (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compd. No.	Amount added (%)				Before flotation	After flotation		
96	None	-	10.0	0	100	45.3	52.5	0.743	87.3
97	None	-	10.0	20	100	45.5	52.2	0.776	85.2
98	None	-	10.0	40	100	44.4	51.9	0.802	82.7
99	None	-	10.0	60	100	43.4	51.7	0.822	79.3
100	b ₁ -1	0.06	7.0	0	100	45.3	58.4	0.091	92.7
101	b ₁ -1	0.06	7.0	20	100	45.2	57.6	0.126	90.8
102	b ₁ -1	0.06	7.0	40	100	44.5	56.3	0.232	88.3
103	b ₁ -1	0.06	7.0	60	100	43.4	53.8	0.497	84.9
104	a ₁ -4	0.10	7.0	20	100	44.9	57.4	0.132	90.8
105	a ₁ -4	0.10	7.0	60	100	43.1	53.5	0.533	84.9
106	b ₁ -11	0.03	7.0	20	100	44.7	57.8	0.125	89.3
107	b ₁ -11	0.03	7.0	60	100	42.9	53.4	0.526	83.4

Note)

The Al³⁺ ion concentrations and the Ca²⁺ ion concentrations in the above Table were determined in flotation.

According to the methods of Test Nos. 100. to 107 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound at a specific pH at a specific Ca^{2+} ion concentration, as compared with those of Test Nos. 96 to 99 (comparative methods), an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp there can be attained. Further, when Al^{3+} ion concentration of the slurry in flotation is 40 ppm or less, it can be expected to obtain qualities superior thereto.

Example I-10

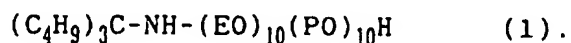
Waste papers (news papers/leaflets = 75/25) recovered in a city were treated according to the following deinking methods, and the performances of the pulp sheet thus obtained were evaluated in the same manner as that in Example I-1. The results thereof are shown in Table I-16.

In this Example, the Ca^{2+} ion concentration of the warm water had been adjusted with CaCl_2 , while the Al^{3+} ion concentration thereof had been adjusted with white water resulting from paper-making.

(1) Test Nos. 108 and 109

To a given amount of waste papers, 1% by weight

(based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide, 0.3% by weight (based on the waste papers) of an EO₁₀/PO₁₀ adduct of an amine represented by the following formula (1) as a deinking agent and warm water were added to prepare a mixture:



The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 5% by weight. The resulting pulp slurry was maintained at 40°C for 60 minutes, and then warm water, of which Al³⁺ ion concentration and Ca²⁺ ion concentration had been suitably adjusted, was added to the pulp slurry to give a pulp slurry having a pulp concentration of 1% by weight, an Al³⁺ ion concentration given in Table I-16 and a Ca²⁺ ion concentration given in Table I-16. Hydrochloric acid was added to the pulp slurry to adjust the pH thereof to a value shown in Table I-16. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation). The pulp slurries were subjected to

paper-making in the same manner as that in Example I-1.

(2) Test Nos. 110 and 111

To a given amount of waste papers, 1% by weight (based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide, 0.2% by weight (based on the waste papers) of an $\text{EO}_{10}/\text{PO}_{10}$ block adduct of stearyl alcohol as a deinking agent and warm water were added to prepare a mixture. The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 5% by weight. The resulting pulp slurry was maintained at 40°C for 60 minutes, and then warm water, of which Al^{3+} ion concentration and Ca^{2+} ion concentration had been suitably adjusted, was added to the pulp slurry to give a pulp slurry having a pulp concentration of 1% by weight, an Al^{3+} ion concentration given in Table I-16 and a Ca^{2+} ion concentration given in Table I-16. In Test No. 110, aluminum sulfate was also added to the pulp slurry to adjust the Al^{3+} concentration of the slurry to a value shown in Table I-16. Then, hydrochloric acid was added to the resulting pulp slurry to adjust the pH

thereof to a value shown in Table I-16. Further, 0.05% by weight (based on the waste papers) of a nonionic polyacrylamide (NP 800, manufactured by Diafloc Co. Ltd.) was added to the pulp slurry. By the addition of the nonionic polyacrylamide, the pH of the resulting pulp slurry was scarcely altered. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation). The pulp slurries were subjected to paper-making in the same manner as that in Example I-1.

(3) Test Nos. 112 to 114

To a given amount of waste papers, 1% by weight (based on the waste papers) of caustic soda, 3% by weight (based on the waste papers) of sodium silicate, 3% by weight (based on the waste papers) of 30% by weight aqueous solution of hydrogen peroxide, 0.2% by weight (based on the waste papers) of an EO₁₀/PO₁₀ block adduct of stearyl alcohol as a deinking agent and warm water were added to prepare a mixture. The waste papers in the mixture were disintegrated at 40°C for 10 minutes to prepare a pulp slurry having a pulp concentration of 5% by weight. The resulting pulp slurry was maintained at 40°C for 60 minutes, and then

warm water, of which Al^{3+} ion concentration and Ca^{2+} ion concentration had been suitably adjusted, was added to the pulp slurry to give a pulp slurry having a pulp concentration of 1% by weight, an Al^{3+} ion concentration given in Table I-16 and a Ca^{2+} ion concentration given in Table I-16. Hydrochloric acid was added to the resulting pulp slurry to adjust the pH thereof to a value shown in Table I-16. Further, 0.06% by weight (based on the waste papers) of a cationic compound shown in Table I-1 or I-2, and Table I-16 was added to the pulp slurry. By the addition of the cationic compound, the pH of the resulting pulp slurry was scarcely altered. After sampling from the resulting pulp slurry (before flotation), the pulp slurry was subjected to flotation at 40°C for 10 minutes to prepare a pulp slurry (after flotation). The pulp slurries were subjected to paper-making in the same manner as that in Example I-1.

Table I-16

Test No.	Nonionic or cationic compound	pH in flotation	Al ³⁺ ion conc. (ppm)	Ca ²⁺ ion conc. (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Name or number of compound				Before flotation	After flotation		
108	None	4.5	30	5	42.2	52.9	0.683	87.8
109	None	7.0	15	200	42.1	52.8	0.690	87.1
110	NP-800	4.5	60	5	44.4	53.6	0.409	77.6
111	NP-800	7.0	15	200	44.6	53.4	0.418	78.2
112	a ₁ - 3	7.0	15	200	45.3	57.7	0.118	91.1
113	b ₁ - 1	7.0	15	200	45.2	57.7	0.126	91.6
114	b ₁ -11	7.0	15	200	45.3	58.1	0.114	91.5

Note)

The Al³⁺ ion concentrations and the Ca²⁺ ion concentrations in the above Table were determined in flotation.

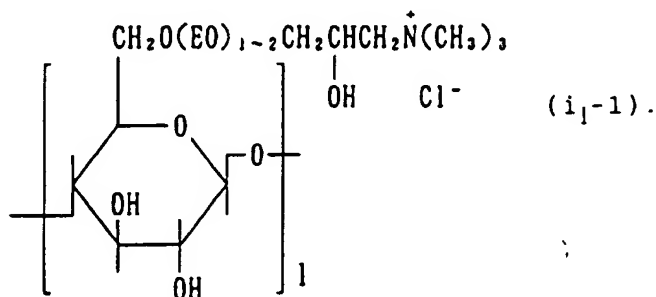
It is observed in Test Nos. 108 and 109 (comparative examples) that a lot of non-liberated ink spots which have not been removed from pulp by flotation is present in the reclaimed paper since the deinking agent having a poor power for liberating ink is used in the disintegrating step of waste papers. Accordingly, the reclaimed pulp is poor in quality. In Test Nos. 110 and 111 (comparative examples), the

addition of the polyacrylamide optionally with aluminum sulfate causes the re-adhesion of ink to cellulose fibers, and reduces the quality of the reclaimed pulp. Further, it is observed that foaming in flotation is extremely enhanced to deteriorate the recovery of pulp.

In contrast, according to the methods of Test Nos. 112 to 114 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound at a specific pH at a specific Ca^{2+} ion concentration and at a specific Al^{3+} ion concentration, an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp are observed.

Example I-11

Deinking test was carried out according to the method described in Example I-1 by using cationic compound i_1-1 represented by the following formula:



The result are shown in Table I-17.

Table I-17

Test No.	Cationic polymer				pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compd. No.	Content of cationic nitrogen* (%)	weight-average molecular weight	Amount added (%)		Before flotation	After flotation		
115	None	-	-	-	10.0	45.0	52.2	0.752	86.8
116	None	-	-	-	9.0	45.4	52.8	0.683	87.2
117	None	-	-	-	8.0	44.9	53.3	0.411	88.3
118	None	-	-	-	7.0	45.6	53.6	0.365	88.9
119	None	-	-	-	6.0	45.0	54.0	0.329	88.9
120	None	-	-	-	5.0	44.6	53.1	0.431	89.1
121	None	-	-	-	4.0	44.3	52.9	0.625	87.6
122	I ₁ -1	1.50	800,000	0.01	9.0	45.2	55.8	0.260	88.7
123	I ₁ -1	1.50	800,000	0.01	8.0	44.6	57.5	0.149	90.5
124	I ₁ -1	1.50	800,000	0.01	7.0	44.7	57.8	0.142	92.7
125	I ₁ -1	1.50	800,000	0.01	6.0	44.6	57.2	0.153	92.4
126	I ₁ -1	1.50	800,000	0.01	5.0	44.4	56.5	0.214	92.1
127	I ₁ -1	1.50	800,000	0.01	4.0	44.4	56.3	0.221	91.0

Note)

*: The content (%) of cationic nitrogen was calculated by multiplying the nitrogen content (%) determined by Kjeldahl method by the ratio of the cationic nitrogen to the total nitrogen which was determined from the molecular formula of the polymer.

In the Tests described above, Test No. 115 is effected in a similar manner as that of a conventional industrial deinking method. According to the methods of Test Nos. 122 to 127 (the methods of the present invention) wherein the flotation is effected in the presence of a cationic compound at a specific pH, as compared with those of Test Nos. 115 to 121 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

<Amines and acid salts thereof>

The amines and acid salts thereof used in the following Examples II-1 to II-10 will be shown in the following Tables II-1 to II-8.

In Tables II-1 to II-8, each numeral in the columns of R_1 to R_3 and W_1 to W_4 means the carbon atom number of a linear alkyl group as a substituent; and "18 Fl", "18 Hyd" and "12 Hyd" refer oleyl group, β -hydroxystearyl group and β -hydroxylauryl group, respectively.

Table II-1

General formula	Compound No.	Substituent		
		R ₁	R ₂	R ₃
$ \begin{array}{c} R_1 \backslash \\ R_2 - N \\ R_3 / \end{array} $	a ₂ - 1	12	H	H
	a ₂ - 2	12	1	1
	a ₂ - 3	12	8	1
	a ₂ - 4	12	12	12
	a ₂ - 5	18	H	H
	a ₂ - 6	18	1	H
	a ₂ - 7	18	2	2
	a ₂ - 8	18	4	4
	a ₂ - 9	18	18	1
	a ₂ -10	18 F1	18 F1	1
	a ₂ -11	18 Hyd	1	1
	a ₂ -12	22	1	H
	a ₂ -13	22	8	1
	a ₂ -14	22	22	1

Table II-2

General formula	Compound No.	Substituent and acid portion			
		R ₁	R ₂	R ₃	HA
$ \begin{array}{c} R_1 \backslash \\ R_2 - N \cdot HA \\ R_3 / \end{array} $	b ₂ - 1	12	H	H	CH ₃ COOH
	b ₂ - 2	12	1	1	HCl
	b ₂ - 3	12	8	1	HCl
	b ₂ - 4	12	12	12	HNO ₃
	b ₂ - 5	18	H	H	H ₂ SO ₄ '
	b ₂ - 6	18	1	H	CH ₃ COOH
	b ₂ - 7	18	2	2	H ₂ SO ₄ '
	b ₂ - 8	18	4	4	HCl
	b ₂ - 9	18	18	1	HCl
	b ₂ -10	18 F1	18 F1	1	HCl
	b ₂ -11	18 Hyd	1	1	HCl
	b ₂ -12	22	1	H	HCl
	b ₂ -13	22	8	1	HCl
	b ₂ -14	22	22	1	HCl

Note)

The sulfuric acid was used in an amount of 1/2 mole per mole of amine.

Table II-3

General formula	Compound No.	Substituent and symbol		
		R ₁	l + m	AO
				EO/PO
$\begin{array}{c} \text{(AO)}_l\text{H} \\ \diagup \\ \text{R}_1\text{N} \\ \diagdown \\ \text{(AO)}_m\text{H} \end{array}$	c ₂ -1	12	4	100/ 0
	c ₂ -2	22	10	0/100
	c ₂ -3	18	100	50/ 50
	c ₂ -4	18	300	100/ 0
	c ₂ -5	22	100	70/ 30

Note)

Ethylene oxide and propylene oxide were added at random.

Table II-4

General formula	Compound No.	Substituent and acid portion	
		R ₁	HA
R ₁ CONHCH ₂ CH ₂ NH ₂ • HA	d ₂ -1	12	HCl
	d ₂ -2	18	CH ₃ COOH
	d ₂ -3	22	H ₂ SO ₄ *
	d ₂ -4	18 F1	HCl
	d ₂ -5	18 Hyd	HCl

Note)

The sulfuric acid was used in an amount of 1/2 mole per mole of amine.

Table II-5

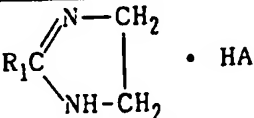
General formula	Compound No.	Substituent and acid portion	
		R ₁	HA
	e ₂ -1	12	HCl
	e ₂ -2	18	HCl
	e ₂ -3	22	HCl

Table II-6

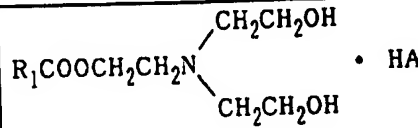
General formula	Compound No.	Substituent and acid portion	
		R ₁	HA
	f ₂ -1	12	HCl
	f ₂ -2	18	HCl
	f ₂ -3	22	HCl

Table II-7

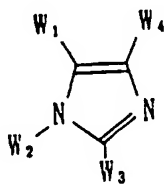
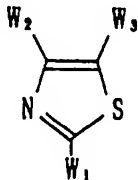
General formula	Compound No.	Substituent			
		W ₁	W ₂	W ₃	W ₄
	g ₂ -1	18	H	H	H
	g ₂ -2	H	18	H	H
	g ₂ -3	1	H	12	1
	g ₂ -4	H	H	H	22
	g ₂ -5	1	12	1	18
	g ₂ -6	H	22	H	2

Table II-8

General formula	Compound No.	Substituent		
		W ₁	W ₂	W ₃
	h ₂ -1	12	H	H
	h ₂ -2	H	18	2
	h ₂ -3	H	1	22

Example II-1

Deinking test was carried out in a similar manner as that in Example I-1 except that the pH of the pulp slurries were each adjusted to a value shown in Table II-9 and that amines and acid salts of amines shown in Tables II-1 and II-2, and Table II-9 were used instead of the cationic compounds. By the addition of the amine or the acid salt of an amine, the pH of the slurry was scarcely altered (the same will be applied to the following Examples II-2 to II-10).

The results thereof are shown in Table II-9.

Table II-9

Test No.	Amine or acid salt of amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
1	None	-	10.0	45.0	52.2	0.752	86.8
2	None	-	9.0	45.4	52.8	0.683	87.2
3	None	-	8.0	44.9	53.3	0.411	88.3
4	None	-	7.0	45.6	53.6	0.365	88.9
5	None	-	6.0	45.0	54.0	0.329	88.9
6	None	-	5.0	44.6	53.1	0.431	89.1
7	None	-	4.0	44.3	52.9	0.625	87.6
8	a ₂ -1	0.10	9.0	45.7	56.0	0.240	89.0
9	a ₂ -1	0.10	8.0	45.3	56.9	0.149	88.7
10	a ₂ -1	0.10	7.0	45.3	57.7	0.144	92.9
11	a ₂ -1	0.10	6.0	45.2	57.3	0.166	92.2
12	a ₂ -1	0.10	5.0	45.0	57.0	0.210	92.5
13	a ₂ -1	0.10	4.0	44.5	56.3	0.227	91.2
14	a ₂ -2	0.06	9.0	45.3	55.9	0.247	89.3
15	a ₂ -2	0.06	8.0	45.0	57.7	0.156	88.9
16	a ₂ -2	0.06	7.0	44.9	57.6	0.147	93.2
17	a ₂ -2	0.06	6.0	44.9	57.1	0.173	92.4
18	a ₂ -2	0.06	5.0	44.6	56.8	0.215	92.8
19	a ₂ -2	0.06	4.0	44.5	56.1	0.233	91.4
20	b ₂ -6	0.03	9.0	45.2	55.6	0.244	87.7
21	b ₂ -6	0.03	8.0	45.0	57.7	0.154	87.3
22	b ₂ -6	0.03	7.0	44.8	57.3	0.149	91.4
23	b ₂ -6	0.03	6.0	44.9	57.1	0.170	90.8
24	b ₂ -6	0.03	5.0	44.5	56.6	0.214	91.3
25	b ₂ -6	0.03	4.0	44.2	56.1	0.230	90.0

Note)

The amount of the amine or acid salt thereof is expressed by % by weight based on the waste

papers (i.e., the absolute dry weight of the waste papers). The same will be applied to the following Examples II-2 to II-10.

In the tests described above, Test No. 1 is effected in a similar manner as that of a conventional industrial deinking method. According to the methods of Test Nos. 8 to 25 (the methods of the present invention) wherein the flotation is effected in the presence of an amine or an acid salt of an amine at a specific pH, as compared with those of Test Nos. 1 to 7 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-2

Deinking test was carried out according to the method described in Example II-1 by using amines shown in Tables II-1 and II-10. The results are shown in Table II-10.

Table II-10

Test No.	Amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
26	None	-	10.0	45.1	52.0	0.754	86.9
27	None	-	7.0	45.3	54.4	0.442	88.9
28	a ₂ -1	0.10	7.0	45.3	57.9	0.139	92.1
29	a ₂ -2	0.10	7.0	45.2	57.7	0.145	92.7
30	a ₂ -3	0.10	7.0	45.0	57.5	0.143	92.7
31	a ₂ -4	0.10	7.0	45.0	56.9	0.151	93.3
32	a ₂ -5	0.10	7.0	45.5	57.8	0.142	92.7
33	a ₂ -6	0.10	7.0	45.6	57.8	0.141	92.4
34	a ₂ -7	0.10	7.0	45.4	57.8	0.136	92.4
35	a ₂ -8	0.10	7.0	45.5	57.6	0.142	92.7
36	a ₂ -9	0.10	7.0	45.0	57.5	0.145	92.1
37	a ₂ -10	0.10	7.0	45.1	57.5	0.155	93.5
38	a ₂ -11	0.10	7.0	45.1	57.3	0.145	93.0
39	a ₂ -12	0.10	7.0	45.3	57.2	0.146	92.6
40	a ₂ -13	0.10	7.0	45.1	57.1	0.148	92.6
41	a ₂ -14	0.10	7.0	44.8	56.8	0.162	93.8
42	a ₂ -1/a ₂ -5	0.05/0.05	7.0	45.3	57.7	0.144	92.7

According to the methods of Test Nos. 28 to 42 (the methods of the present invention) wherein the flotation is effected in the presence of an amine shown in Table II-1 at a specific pH, as compared with those of Test Nos. 26 and 27 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an

increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-3

Deinking test was carried out according to the method described in Example II-1 by using acid salts of amines shown in Tables II-2 and II-11, optionally together with amine a₂-10 shown in Table II-1. The results are shown in Table II-11.

Table II-11

Test No.	Amine and acid salt of amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
43	None	-	10.0	45.1	52.1	0.749	86.8
44	None	-	7.0	45.3	54.2	0.449	88.7
45	b ₂ -1	0.05	7.0	45.3	57.2	0.184	92.0
46	b ₂ -1	0.10	7.0	45.2	57.9	0.145	92.7
47	b ₂ -1	0.20	7.0	45.0	58.9	0.101	93.5
48	b ₂ -2	0.10	7.0	45.1	57.5	0.144	92.6
49	b ₂ -3	0.10	7.0	44.9	57.7	0.142	92.6
50	b ₂ -4	0.10	7.0	45.1	56.7	0.157	93.4
51	b ₂ -5	0.10	7.0	45.4	58.0	0.132	92.6
52	b ₂ -6	0.10	7.0	45.5	57.6	0.138	92.3
53	b ₂ -7	0.10	7.0	45.3	58.0	0.135	92.2
54	b ₂ -8	0.10	7.0	45.4	57.4	0.143	92.8
55	b ₂ -9	0.10	7.0	45.1	57.7	0.138	92.6
56	b ₂ -10	0.10	7.0	45.0	57.3	0.145	93.3
57	b ₂ -11	0.10	7.0	45.2	57.5	0.139	92.9
58	b ₂ -12	0.10	7.0	45.2	57.0	0.148	92.8
59	b ₂ -13	0.10	7.0	45.2	56.9	0.151	92.7
60	b ₂ -14	0.10	7.0	44.7	56.6	0.164	93.9
61	b ₂ -2/a ₂ -10	0.05/0.05	7.0	45.4	57.7	0.139	92.5

According to the methods of Test Nos. 45 to 61 (the methods of the present invention) wherein the flotation is effected in the presence of an acid salt of an amine shown in Table II-2 optionally together with amine a₂-10 shown in Table II-1 at a specific pH, as compared with those of Test Nos. 43 and 44 (comparative methods), there can be expected to attain

an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-4

Deinking test was carried out according to the method described in Example II-1 by using amines shown in Tables II-3 and II-12. An EO₂₀ adduct of stearic acid was used as the deinking agent in the present Example. The results are shown in Table II-12.

Table II-12

Test No.	Amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
62	None	-	10.0	45.2	52.1	0.769	86.9
63	None	-	7.0	45.5	54.1	0.462	88.1
64	c ₂ -1	0.05	7.0	45.4	57.8	0.138	92.8
65	c ₂ -2	0.05	7.0	44.7	56.6	0.193	93.9
66	c ₂ -3	0.05	7.0	45.0	58.0	0.140	92.2
67	c ₂ -4	0.05	7.0	45.6	58.1	0.134	92.9
68	c ₂ -5	0.05	7.0	45.6	58.0	0.138	92.2

According to the methods of Test Nos. 64 to 68 (the methods of the present invention) wherein the flotation is effected in the presence of an amine shown in Table II-3 at a specific pH, as compared with

those of Test Nos. 62 and 63 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-5

Deinking test was carried out according to the method described in Example II-1 by using acid salts of amines shown in Tables II-4 to II-6, and Table II-13. An EO₆₀ adduct of a mixture (1:1 by mole) of beef tallow and glycerol was used as the deinking agent in the present Example. The results are shown in Table II-13.

Table II-13

Test No.	Acid salt of amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
69	None	-	10.0	45.0	53.1	0.709	85.9
70	None	-	7.0	45.4	54.6	0.411	86.1
71	d ₂ -1	0.10	7.0	44.9	57.4	0.139	91.7
72	d ₂ -2	0.10	7.0	45.3	57.6	0.139	92.9
73	d ₂ -3	0.10	7.0	45.2	56.9	0.146	92.2
74	d ₂ -4	0.10	7.0	45.0	56.7	0.156	93.5
75	d ₂ -5	0.10	7.0	45.1	57.0	0.147	91.7
76	e ₂ -1	0.10	7.0	45.1	57.4	0.140	92.2
77	e ₂ -2	0.10	7.0	45.2	57.6	0.144	92.7
78	e ₂ -3	0.10	7.0	45.4	57.2	0.153	93.3
79	f ₂ -1	0.10	7.0	44.8	57.3	0.148	92.4
80	f ₂ -2	0.10	7.0	45.2	57.4	0.145	92.8
81	f ₂ -3	0.10	7.0	45.5	56.7	0.159	93.3

According to the methods of Test Nos. 71 to 81 (the methods of the present invention) wherein the flotation is effected in the presence of an acid salt of an amine shown in Table II-4, II-5 or II-6 at a specific pH, as compared with those of Test Nos. 69 and 70 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-6

Deinking test was carried out according to the method described in Example II-1 by using amines shown in Tables II-7 and II-8, and Table II-14. The results are shown in Table II-14.

Table II-14

Test No.	Amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
82	None	-	10.0	45.0	52.0	0.752	86.6
83	None	-	7.0	45.4	54.3	0.444	88.4
84	g ₂ -1	0.10	7.0	45.2	58.0	0.134	92.2
85	g ₂ -2	0.10	7.0	45.2	58.2	0.130	92.1
86	g ₂ -3	0.10	7.0	45.1	58.1	0.131	92.0
87	g ₂ -4	0.10	7.0	44.9	57.9	0.141	92.8
88	g ₂ -5	0.10	7.0	45.3	57.8	0.142	92.5
89	g ₂ -6	0.10	7.0	44.9	57.7	0.145	92.1
90	h ₂ -1	0.10	7.0	45.4	58.2	0.131	92.1
91	h ₂ -2	0.10	7.0	45.2	57.9	0.142	92.4
92	h ₂ -3	0.10	7.0	45.0	57.5	0.144	92.8

According to the methods of Test Nos. 84 to 92 (the methods of the present invention) wherein the flotation is effected in the presence of an amine shown in Table II-7 or II-8 at a specific pH, as compared with those of Test Nos. 82 and 83 (comparative methods), there can be expected to attain

an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-7

Deinking test was carried out in a similar manner as that in Example I-7 except that the pH of the pulp slurries were each adjusted to a value shown in Table II-15 and that amines and acid salts of amines shown in Tables II-1, II-2 and II-3, and Table II-15 were used instead of the cationic compounds. The results thereof are shown in Table II-15.

Table II-15

Test No.	Deinking agent No. (See Table I-12)	Amine and acid salt of amine		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
		Compd. No.	Amount added (%)		Before flotation	After flotation		
93	A1	None	-	10.0	43.9	51.0	0.841	88.5
94	A2	None	-	10.0	44.0	52.2	0.785	86.5
95	A3	None	-	10.0	44.6	52.1	0.771	86.2
96	A4	None	-	10.0	47.8	53.5	0.415	90.0
97	A1	a ₂ -1	0.10	7.0	44.4	56.5	0.196	92.4
98	A2	a ₂ -2	0.10	7.0	44.6	57.8	0.149	91.1
99	A3	b ₂ -6	0.10	7.0	44.8	57.4	0.157	90.4
100	A4	c ₂ -1	0.05	7.0	47.3	58.9	0.142	94.2

According to the methods of Test Nos. 97 to 100 (the methods of the present invention) wherein various deinking agents are each used and the flotation is effected in the presence of an amine or an acid salt of an amine at a specific pH, as compared with those of Test Nos. 93 to 96 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example II-8

Deinking test was carried out in a similar manner as that in Example I-8 except that the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table II-16 and that amines and acid salts of amines shown in Tables II-1 and II-2, and Table II-16 were used instead of the cationic compounds.

The results thereof are shown in Table II-16.

Table II-16

Test No.	Amine and acid salt of amine		pH in flotation	Ca ²⁺ ion concentration (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)			Before flotation	After flotation		
101	None	-	10.0	0	44.8	52.1	0.770	86.4
102	None	-	10.0	50	45.0	52.2	0.752	86.8
103	None	-	10.0	100	45.3	52.5	0.743	87.3
104	None	-	10.0	200	45.2	52.6	0.739	87.3
105	None	-	10.0	400	45.0	52.3	0.765	87.6
106	None	-	10.0	800	44.7	51.8	0.781	87.6
107	a ₂ -1	0.10	7.0	0	45.3	57.7	0.144	92.9
108	a ₂ -1	0.10	7.0	50	45.5	58.0	0.126	92.3
109	a ₂ -1	0.10	7.0	100	45.8	58.8	0.071	92.1
110	a ₂ -1	0.10	7.0	200	45.9	59.6	0.065	92.3
111	a ₂ -1	0.10	7.0	400	45.6	58.1	0.106	93.2
112	a ₂ -1	0.10	7.0	800	45.4	57.2	0.178	94.1
113	a ₂ -2	0.06	7.0	0	44.9	57.6	0.147	93.2
114	a ₂ -2	0.06	7.0	200	45.4	59.5	0.066	92.6
115	a ₂ -2	0.06	7.0	800	44.9	57.2	0.181	93.8
116	b ₂ -6	0.03	7.0	0	44.8	57.3	0.149	91.4
117	b ₂ -6	0.03	7.0	200	45.2	59.1	0.075	90.8
118	b ₂ -6	0.03	7.0	800	44.8	56.8	0.189	92.6

Note)

The Ca²⁺ ion concentrations in the above Table were determined in flotation.

According to the methods of Test Nos. 107 to 118 (the methods of the present invention) wherein the flotation is effected in the presence of an amine or an acid salt of an amine at a specific pH at a specific Ca^{2+} ion concentration, as compared with those of Test Nos. 101 to 106 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example II-9

Deinking test was carried out in a similar manner as that in Example I-9 except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table II-17 and that amines and acid salts of amines shown in Tables II-1 and II-2, and Table II-17 were used instead of the cationic compounds. For the adjustment of the Ca^{2+} ion concentration, CaCl_2 was used, and for the adjustment of Al^{3+} ion concentration, white water resulting from paper-making, or the white water and aluminum sulfate (in Test Nos. 122, 126 and 130) was(were) used. Further, for the adjustment of pH, hydrochloric acid or sodium hydroxide was used.

The results thereof are shown in Table II-17.

Table II-17

Test No.	Amine and acid salt of amine		pH in flotation	Al ³⁺ ion conc. (ppm)	Ca ²⁺ ion conc. (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compd. No.	Amount added (%)				Before flotation	After flotation		
119	None	-	10.0	0	100	45.3	52.5	0.743	87.3
120	None	-	10.0	20	100	45.5	52.2	0.776	85.2
121	None	-	10.0	40	100	44.4	51.9	0.802	82.7
122	None	-	10.0	60	100	43.4	51.7	0.822	79.3
123	a ₂ -1	0.10	7.0	0	100	45.8	58.8	0.071	92.1
124	a ₂ -1	0.10	7.0	20	100	45.9	58.0	0.106	90.2
125	a ₂ -1	0.10	7.0	40	100	45.2	56.7	0.212	87.7
126	a ₂ -1	0.10	7.0	60	100	44.1	54.0	0.387	84.3
127	a ₂ -2	0.06	7.0	20	100	45.4	57.7	0.107	90.6
128	a ₂ -2	0.06	7.0	60	100	43.9	53.8	0.489	84.5
129	b ₂ -6	0.03	7.0	20	100	45.1	57.3	0.116	88.6
130	b ₂ -6	0.03	7.0	60	100	43.5	53.6	0.505	82.9

Note)

The Al³⁺ ion concentrations and the Ca²⁺ ion concentrations in the above Table were determined in flotation.

According to the methods of Test Nos. 123 to 130 (the methods of the present invention) wherein the

flotation is effected in the presence of an amine or an acid salt of an amine at a specific pH at a specific Ca^{2+} ion concentration, as compared with those of Test Nos. 119 to 122 (comparative methods), an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp there can be attained. Further, when Al^{3+} ion concentration of the slurry in flotation is 40 ppm or less, it can be expected to obtain qualities superior thereto.

Example II-10

Waste papers (news papers/leaflets = 75/25) recovered in a city were treated according to the following deinking methods, and the performances of the pulp sheet thus obtained were evaluated in the same manner as that in Example I-1. The results thereof are shown in Table II-18.

In this Example, the Ca^{2+} ion concentration of the warm water had been adjusted with CaCl_2 , while the Al^{3+} ion concentration thereof had been adjusted with white water resulting from paper-making.

(1) Test Nos. 131 and 132

The pulp sheet were prepared in a similar manner as that in Example I-10-(1) except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH

of the pulp slurries were each adjusted to a value shown in Table II-18.

(2) Test Nos. 133 and 134

The pulp sheet were prepared in a similar manner as that in Example I-10-(2) except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table II-18. In Test No. 133, aluminum sulfate was also added to the pulp slurry to adjust the Al^{3+} concentration of the slurry to a value shown in Table II-18.

(3) Test Nos. 135 and 136

The pulp sheet were prepared in a similar manner as that in Example I-10-(3) except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table II-18 and that 0.1% by weight (based on the waste papers) of amine a_2-1 shown in Table II-1 or acid salt of amine b_2-5 shown in Table II-2 was used instead of the cationic compound.

Table II-18

Test No.	Nonionic compound, amine or acid salt of amine	pH in flotation	Al ³⁺ ion conc. (ppm)	Ca ²⁺ ion conc. (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Name or number of compound				Before flotation	After flotation		
131	None	4.5	30	5	42.2	52.9	0.683	87.8
132	None	7.0	15	200	42.1	52.8	0.690	87.1
133	NP-800	4.5	60	5	44.4	53.6	0.409	77.6
134	NP-800	7.0	15	200	44.6	53.4	0.418	78.2
135	a ₂ -1	7.0	15	200	45.5	58.8	0.106	91.3
136	b ₂ -5	7.0	15	200	45.4	58.9	0.112	91.6

Note)

The Al³⁺ ion concentrations and the Ca²⁺ ion concentrations in the above Table were determined in flotation.

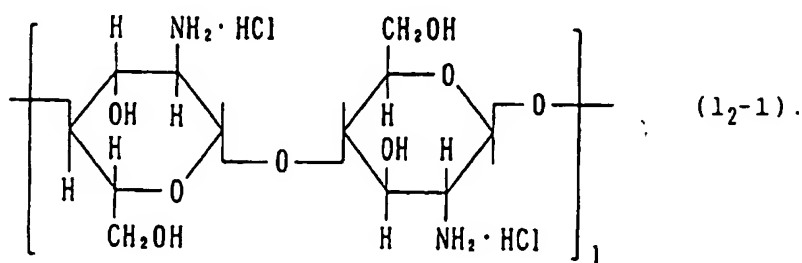
It is observed in Test Nos. 131 and 132 (comparative examples) that a lot of non-liberated ink spots which have not been removed from pulp by flotation is present in the reclaimed paper since the deinking agent having a poor power for liberating ink is used in the disintegrating step of waste papers. Accordingly, the reclaimed pulp is poor in quality. In Test Nos. 133 and 134 (comparative examples), the addition of the polyacrylamide optionally with

aluminum sulfate causes the re-adhesion of ink to cellulose fibers, and reduces the quality of the reclaimed pulp. Further, it is observed that foaming in flotation is extremely enhanced to deteriorate the recovery of pulp.

In contrast, according to the methods of Test Nos. 134 and 135 (the methods of the present invention) wherein the flotation is effected in the presence of an amine or an acid salt of an amine at a specific pH at a specific Ca^{2+} ion concentration and at a specific Al^{3+} ion concentration, an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp are observed.

Example II-11

Deinking test was carried out according to the method described in Example II-1 by using an acid salt of an amine represented by the following formula:



The results are shown in Table II-19.

Table II-19

Test No.	Polymer				pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compd. No.	Content of nitrogen derived from amino groups* (%)	weight-average molecular weight	Amount added (%)		Before flotation	After flotation		
137	None	-	-	-	10.0	45.0	52.2	0.752	86.8
138	None	-	-	-	9.0	45.4	52.8	0.683	87.2
139	None	-	-	-	8.0	44.9	53.3	0.411	88.3
140	None	-	-	-	7.0	45.6	53.6	0.365	88.9
141	None	-	-	-	6.0	45.0	54.0	0.329	88.9
142	None	-	-	-	5.0	44.6	53.1	0.431	89.1
143	None	-	-	-	4.0	44.3	52.9	0.625	87.6
144	1 ₂ -1	6.40	300,000	0.01	9.0	45.3	54.6	0.302	88.9
145	1 ₂ -1	6.40	300,000	0.01	8.0	44.8	56.8	0.178	90.7
146	1 ₂ -1	6.40	300,000	0.01	7.0	45.0	57.0	0.165	92.8
147	1 ₂ -1	6.40	300,000	0.01	6.0	44.9	56.7	0.192	92.0
148	1 ₂ -1	6.40	300,000	0.01	5.0	44.7	56.1	0.248	91.5
149	1 ₂ -1	6.40	300,000	0.01	4.0	44.6	55.8	0.286	90.3

Note)

*: The content (%) of nitrogen derived from amino groups was calculated by multiplying the nitrogen content (%) determined by Kjeldahl method by the ratio of the nitrogen derived from amino groups to the total nitrogen which was determined from the molecular formula of the polymer.

In the tests described above, Test No. 137 is effected in a similar manner as that of a conventional industrial deinking method. According to the methods of Test Nos. 144 to 149 (the methods of the present invention) wherein the flotation is effected in the presence of an amine or an acid salt of an amine at a specific pH, as compared with those of Test Nos. 137 to 143 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

<Amphoteric compounds>

The amphoteric compounds used in the following Examples III-1 to III-16 will be shown in the following Tables III-1 to III-12.

In Tables III-1 to III-12, each numeral in the columns of R_1 to R_4 means the carbon atom number of a linear alkyl group as a substituent; and "18 F1", "18 Hyd" and "12 Hyd" refer oleyl group, β -hydroxystearyl group and β -hydroxylauryl group, respectively.

Table III-1

General formula	Compound No.	Substituent		
		R ₁	R ₂	R ₃
$\begin{array}{c} R_1 \backslash \\ R_2 - N \rightarrow O \\ R_3 / \end{array}$	a ₃ -1	12	1	1
	a ₃ -2	18	18	1
	a ₃ -3	18	2	2
	a ₃ -4	18 F1	8	1
	a ₃ -5	22	12	12

Table III-2

General formula	Compound No.	Substituent		
		R ₁	R ₂	R ₃
$\begin{array}{c} R_1 \backslash \\ R_2 - N^+ CH_2 COO^- \\ R_3 / \end{array}$	b ₃ -1	12	1	1
	b ₃ -2	18	18	1
	b ₃ -3	18	2	2
	b ₃ -4	18 F1	8	1
	b ₃ -5	22	12	12

Table III-3

General formula	Compound No.	Substituent		
		R ₅ in Y ₁	R ₅ in Y ₂	M
$\begin{array}{c} Y_1 \backslash \\ NCH_2 COOM \\ Y_2 / \end{array}$	c ₃ -1	12	18	H
	c ₃ -2	18	H	Na
	c ₃ -3	18 F1	1	NH ₄

Table III-4

General formula	Compound No.	Substituent	
		R ₄	M
$\text{R}_4\text{CONHCH}_2\text{CH}_2\text{N} \begin{array}{l} \diagup \text{CH}_2\text{COOM} \\ \diagdown \text{CH}_2\text{COOM} \end{array}$	d ₃ -1	12	Na
	d ₃ -2	18	Na
	d ₃ -3	22	NH ₄
	d ₃ -4	18 F1	Na
	d ₃ -5	18 Hyd	Na

Table III-5

General formula	Compound No.	Substituent	
		R ₄	M
$\text{R}_4\text{N} \begin{array}{l} \diagup \text{CH}_2\text{COOM} \\ \diagdown \text{CH}_2\text{COO}^- \end{array}$	e ₃ -1	12	Na
	e ₃ -2	18	Na
	e ₃ -3	22	NH ₄
	e ₃ -4	18 F1	Na
	e ₃ -5	18 Hyd	Na

Table III-6

General formula	Compound No.	Substituent		
		R ₄	Z ₁	Z ₂
$\text{R}_4\text{N} \begin{array}{l} \diagup \text{Z}_1 \\ \diagdown \text{Z}_2 \end{array}$	f ₃ -1	12	CH ₂ COONa	CH ₂ COONa
	f ₃ -2	18	CH ₂ COOH	H
	f ₃ -3	22	CH ₂ COOH	CH ₂ COOH
	f ₃ -4	18 F1	CH ₂ COOH	H
	f ₃ -5	18 Hyd	CH ₂ COOH	H

Table III-7

General formula	Compound No.	Substituent	
		R ₄	M
$R_4NHCH_2CH_2COOM$	g ₃ -1	12	Na
	g ₃ -2	18	Na
	g ₃ -3	22	NH ₄
	g ₃ -4	18 F1	Na
	g ₃ -5	18 Hyd	Na

Table III-8

General formula	Compound No.	Substituent	
		R ₄	M
$R_4NH(CH_2)_5COOM$	h ₃ -1	12	Na
	h ₃ -2	18	Na
	h ₃ -3	22	NH ₄
	h ₃ -4	18 F1	Na
	h ₃ -5	18 Hyd	Na

Table III-9

General formula	Compound No.	Substituent		
		R ₁	R ₂	R ₃
$ \begin{array}{c} R_1 \backslash \\ R_2 - N^+ \\ R_3 / \quad \backslash \\ \quad \quad CHCOO^- \\ \quad \quad \\ \quad \quad CH_2COOH \end{array} $	i ₃ -1	12	1	1
	i ₃ -2	18	18	1
	i ₃ -3	18	2	2
	i ₃ -4	18 F1	8	1
	i ₃ -5	22	12	12

Table III-10

General formula	Compound No.	Substituent
		R ₄
$ \begin{array}{c} \text{R}_4 - \text{C} = \text{N} - \text{CH}_2 \\ \quad \quad \quad \\ \quad \quad \quad \text{N}^+ - \text{CH}_2 \\ \quad \quad \quad \\ \text{CH}_2\text{COO}^- \quad \quad \quad \text{CH}_2\text{CH}_2\text{OH} \end{array} $	j ₃ -1	12
	j ₃ -2	18
	j ₃ -3	22
	j ₃ -4	18 F1
	j ₃ -5	18 Hyd

Table III-11

	Compound No.	Kind of compound
Phospholipid	k ₃ -1	Soybean lecithin
	k ₃ -2	Phosphatidyl choline derived from egg
	k ₃ -3	Phosphatidyl ethanolamine derived from soybean

Table III-12

	Compound No.	Kind of compound
Protein	l ₃ -1	Soybean protein
	l ₃ -2	Casein
	l ₃ -3	Lactalbumin

Example III-1

Deinking test was carried out in a similar manner as that in Example I-1 except that the pH of the pulp slurries were each adjusted to a value shown in Table III-13 and that amphoteric compounds shown in Tables III-1, III-2 and III-3, and Table III-13 were used instead of the cationic compounds. By the addition of the amphoteric compound, the pH of the slurry was scarcely altered (the same will be applied to the following Examples III-2 to III-16).

The results thereof are shown in Table III-13.

Table III-13

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
1	None	-	10.0	45.0	52.2	0.752	86.8
2	None	-	9.0	45.4	52.8	0.683	87.2
3	None	-	8.0	44.9	53.3	0.411	88.3
4	None	-	7.0	45.6	53.6	0.365	88.9
5	None	-	6.0	45.0	54.0	0.329	88.9
6	None	-	5.0	44.6	53.1	0.431	89.1
7	None	-	4.0	44.3	52.9	0.625	87.6
8	a ₃ -1	0.06	9.0	45.0	56.2	0.258	89.0
9	a ₃ -1	0.06	8.0	44.9	57.9	0.157	89.0
10	a ₃ -1	0.06	7.0	44.9	57.7	0.155	93.0
11	a ₃ -1	0.06	6.0	44.9	57.3	0.186	92.3
12	a ₃ -1	0.06	5.0	44.9	57.1	0.226	92.7
13	a ₃ -1	0.06	4.0	44.8	56.5	0.246	91.2
14	b ₃ -1	0.06	9.0	45.0	56.3	0.253	88.9
15	b ₃ -1	0.06	8.0	45.0	57.2	0.152	88.7
16	b ₃ -1	0.06	7.0	44.9	56.9	0.151	92.8
17	b ₃ -1	0.06	6.0	44.9	56.6	0.172	92.3
18	b ₃ -1	0.06	5.0	44.8	56.5	0.220	92.3
19	b ₃ -1	0.06	4.0	44.8	56.4	0.248	91.2
20	c ₃ -2	0.06	9.0	45.1	55.9	0.239	87.7
21	c ₃ -2	0.06	8.0	45.0	57.0	0.150	87.2
22	c ₃ -2	0.06	7.0	44.9	57.2	0.144	91.3
23	c ₃ -2	0.06	6.0	44.9	57.4	0.141	90.7
24	c ₃ -2	0.06	5.0	44.7	57.3	0.150	91.1
25	c ₃ -2	0.06	4.0	44.5	56.7	0.216	89.7

Note)

The amount of the amphoteric compound is expressed by % by weight based on the waste

papers (i.e., the absolute dry weight of the waste papers). The same will be applied to the following Examples III-2 to III-16.

In the tests described above, Test No. 1 is effected in a similar manner as that of a conventional industrial deinking method. According to the methods of Test Nos. 8 to 25 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound at a specific pH, as compared with those of Test Nos. 1 to 7 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example III-2

Deinking test was carried out according to the method described in Example III-1 by using amphoteric compounds shown in Tables III-1 and III-14. The results are shown in Table III-14.

Table III-14

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
26	None	-	10.0	45.2	52.1	0.769	86.8
27	None	-	7.0	45.4	54.5	0.429	88.7
28	a _j -1	0.10	7.0	44.9	58.1	0.135	91.9
29	a _j -2	0.10	7.0	45.0	57.4	0.146	93.7
30	a _j -3	0.10	7.0	45.2	57.6	0.138	92.6
31	a _j -4	0.10	7.0	44.6	57.2	0.155	93.5
32	a _j -5	0.10	7.0	45.2	57.1	0.159	93.4

According to the methods of Test Nos. 28 to 32 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-1 at a specific pH, as compared with those of Test Nos. 26 and 27 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-3

Deinking test was carried out according to the method described in Example III-1 by using amphoteric compounds shown in Tables III-2 and III-15. The results are shown in Table III-15.

Table III-15

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation	After flotation	
33	None	-	10.0	45.1	52.3	0.757	86.6
34	None	-	7.0	45.4	54.4	0.434	88.8
35	b ₃ -1	0.10	7.0	45.1	58.0	0.136	91.8
36	b ₃ -2	0.10	7.0	45.1	57.5	0.145	93.4
37	b ₃ -3	0.10	7.0	45.0	57.5	0.146	92.4
38	b ₃ -4	0.10	7.0	44.9	57.1	0.152	93.5
39	b ₃ -5	0.10	7.0	45.2	57.1	0.155	93.6

According to the methods of Test Nos. 35 to 39 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-2 at a specific pH, as compared with those of Test Nos. 33 and 34 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-4

Deinking test was carried out according to the method described in Example III-1 by using amphoteric compounds shown in Tables III-3 and III-16. An EO₂₀ adduct of stearic acid was used as the deinking agent in the present Example. The results are shown in

Table III-16.

Table III-16

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
40	None	-	10.0	45.1	52.1	0.767	86.6
41	None	-	7.0	45.3	54.3	0.436	88.7
42	C ₃ -1	0.10	7.0	45.4	57.4	0.144	92.2
43	C ₃ -2	0.10	7.0	45.3	58.0	0.136	91.9
44	C ₃ -5	0.10	7.0	45.4	57.8	0.140	92.1

According to the methods of Test Nos. 42 to 44 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-3 at a specific pH, as compared with those of Test Nos. 40 and 41 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-5

Deinking test was carried out according to the method described in Example III-1 by using amphoteric compounds shown in Table III-4 and III-17. An EO₆₀ adduct of a mixture (1:1 by mole) of beef tallow and

glycerol was used as the deinking agent in the present Example. The results are shown in Table III-17.

Table III-17

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
45	None	-	10.0	45.2	52.3	0.755	86.5
46	None	-	7.0	45.2	54.1	0.441	88.6
47	d ₃ -1	0.10	7.0	45.2	58.0	0.137	91.5
48	d ₃ -2	0.10	7.0	45.1	57.4	0.145	91.8
49	d ₃ -3	0.10	7.0	45.3	57.3	0.151	92.2
50	d ₃ -4	0.10	7.0	44.9	57.1	0.158	92.1
51	d ₃ -5	0.10	7.0	45.1	57.5	0.140	92.6

According to the methods of Test Nos. 47 to 51 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-4 at a specific pH, as compared with those of Test Nos. 45 and 46 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-6

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-5 and III-18. The results are shown in Table III-18.

Table III-18

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
52	None	-	10.0	45.3	52.1	0.760	86.5
53	None	-	7.0	45.2	54.3	0.433	89.0
54	e ₃ -1	0.10	7.0	45.3	57.7	0.144	91.4
55	e ₃ -2	0.10	7.0	45.3	57.5	0.145	92.0
56	e ₃ -3	0.10	7.0	45.2	57.6	0.146	92.1
57	e ₃ -4	0.10	7.0	45.2	57.4	0.147	92.5
58	e ₃ -5	0.10	7.0	45.2	57.4	0.146	92.6

According to the methods of Test Nos. 54 to 58 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-5 at a specific pH, as compared with those of Test Nos. 52 and 53 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-7

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-6 and III-19. The results are shown in Table III-19.

Table III-19

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
59	None	-	10.0	45.2	52.1	0.761	86.5
60	None	-	7.0	45.3	54.4	0.439	88.7
61	f ₃ -1	0.10	7.0	45.2	57.6	0.145	91.7
62	f ₃ -2	0.10	7.0	45.2	57.3	0.148	92.2
63	f ₃ -3	0.10	7.0	45.3	57.5	0.146	92.3
64	f ₃ -4	0.10	7.0	45.1	57.6	0.147	92.1
65	f ₃ -5	0.10	7.0	45.2	57.5	0.147	92.4

According to the methods of Test Nos. 61 to 65 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-6 at a specific pH, as compared with those of Test Nos. 59 and 60 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-8

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-7 and III-20. The results are shown in Table III-20.

Table III-20

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation	After flotation	
66	None	-	10.0	45.1	52.1	0.754	86.5
67	None	-	7.0	45.3	54.2	0.439	88.9
68	9 ₃ -1	0.10	7.0	45.2	57.8	0.137	92.3
69	9 ₃ -2	0.10	7.0	45.2	57.7	0.145	92.9
70	9 ₃ -3	0.10	7.0	45.3	57.5	0.147	93.1
71	9 ₃ -4	0.10	7.0	45.0	57.3	0.156	93.4
72	9 ₃ -5	0.10	7.0	45.1	57.5	0.150	93.1

According to the methods of Test Nos. 68 to 72 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-7 at a specific pH, as compared with those of Test Nos. 66 and 67 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-9

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-8 and III-21. The results are shown in Table III-21.

Table III-21

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
73	None	-	10.0	45.1	52.2	0.759	86.7
74	None	-	7.0	45.4	54.4	0.435	88.7
75	h ₃ -1	0.10	7.0	45.1	57.6	0.146	92.2
76	h ₃ -2	0.10	7.0	45.1	57.5	0.144	92.3
77	h ₃ -3	0.10	7.0	45.1	57.4	0.146	92.8
78	h ₃ -4	0.10	7.0	45.2	57.1	0.162	93.1
79	h ₃ -5	0.10	7.0	45.0	57.5	0.145	92.4

According to the methods of Test Nos. 75 to 79 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-8 at a specific pH, as compared with those of Test Nos. 73 and 74 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-10

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-9 and III-22. The results are shown in Table III-22.

Table III-22

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
80	None	-	10.0	45.2	52.2	0.766	86.7
81	None	-	7.0	45.1	54.4	0.435	88.7
82	i ₃ -1	0.10	7.0	45.2	57.7	0.141	91.8
83	i ₃ -2	0.10	7.0	45.1	57.4	0.147	92.4
84	i ₃ -3	0.10	7.0	45.0	57.4	0.146	92.5
85	i ₃ -4	0.10	7.0	45.1	57.6	0.143	92.6
86	i ₃ -5	0.10	7.0	45.4	57.6	0.142	92.1

According to the methods of Test Nos. 82 to 86 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-9 at a specific pH, as compared with those of Test Nos. 80 and 81 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-11

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-10 and III-23. The results are shown in Table III-23.

Table III-23

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation	After flotation	
87	None	-	10.0	45.2	52.4	0.754	86.7
88	None	-	7.0	45.2	54.3	0.440	88.6
89	j ₃ -1	0.10	7.0	45.2	57.6	0.142	92.3
90	j ₃ -2	0.10	7.0	45.3	57.4	0.150	92.4
91	j ₃ -3	0.10	7.0	45.1	57.3	0.153	92.2
92	j ₃ -4	0.10	7.0	45.0	57.6	0.147	91.5
93	j ₃ -5	0.10	7.0	45.2	57.7	0.141	91.6

According to the methods of Test Nos. 89 to 93 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-10 at a specific pH, as compared with those of Test Nos. 87 and 88 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-12

Deinking test was carried out according to the method described in Example III-1 by using amphoteric

compounds shown in Tables III-11 and III-12, and Table III-24. The results are shown in Table III-24.

Table III-24

Test No.	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)		Before flotation	After flotation		
94	None	-	10.0	45.2	52.2	0.763	86.5
95	None	-	7.0	45.4	54.3	0.439	88.6
96	k ₃ -1	0.30	7.0	45.3	57.9	0.136	91.8
97	k ₃ -2	0.30	7.0	45.4	57.8	0.138	91.4
98	k ₃ -3	0.30	7.0	45.3	57.9	0.136	91.4
99	l ₃ -1	0.30	7.0	45.4	58.0	0.135	91.0
100	l ₃ -2	0.30	7.0	45.5	57.5	0.142	92.2
101	l ₃ -3	0.30	7.0	45.2	57.5	0.143	92.4

According to the methods of Test Nos. 96 to 101 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound shown in Table III-11 or III-12 at a specific pH, as compared with those of Test Nos. 94 and 95 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-13

Deinking test was carried out in a similar manner

as that in Example I-7 except that the pH of the pulp slurries were each adjusted to a value shown in Table III-25 and that amphoteric compounds shown in Tables III-1, III-2 and III-3, and Table III-25 were used instead of the cationic compounds. The results thereof are shown in Table III-25.

Table III-25

Test No.	Deinking agent No. (See Table I-12)	Amphoteric compound		pH in flotation	Whiteness (%)		Residual ink area ratio (%) After flotation	Recovery of pulp (%)
		Compd. No.	Amount added (%)		Before flotation	After flotation		
102	A1	None	-	10.0	43.9	51.0	0.841	88.5
103	A2	None	-	10.0	44.0	52.2	0.785	86.5
104	A3	None	-	10.0	44.6	52.1	0.771	86.2
105	A4	None	-	10.0	47.8	53.5	0.415	90.0
106	A1	a ₃ -1	0.10	7.0	44.2	56.2	0.210	91.5
107	A2	a ₃ -2	0.10	7.0	44.3	57.3	0.158	90.4
108	A3	b ₃ -6	0.10	7.0	44.6	57.1	0.166	89.5
109	A4	c ₃ -1	0.05	7.0	47.0	58.1	0.161	93.4

According to the methods of Test Nos. 106 to 109 (the methods of the present invention) wherein various deinking agents are each used and the flotation is effected in the presence of an amphoteric compound at a specific pH, as compared with those of Test Nos. 102

to 105 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp.

Example III-14

Deinking test was carried out in a similar manner as that in Example I-8 except that the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table III-26 and that amphoteric compounds shown in Tables III-1, III-2 and III-3, and Table III-26 were used instead of the cationic compounds.

The results thereof are shown in Table III-26.

Table III-26

Test No.	Amphoteric compound		pH in flotation	Ca ²⁺ ion concentration (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compound No.	Amount added (%)			Before flotation	After flotation		
110	None	-	10.0	0	44.8	52.1	0.770	86.4
111	None	-	10.0	50	45.0	52.2	0.752	86.8
112	None	-	10.0	100	45.3	52.5	0.743	87.3
113	None	-	10.0	200	45.2	52.6	0.739	87.3
114	None	-	10.0	400	45.0	52.3	0.765	87.6
115	None	-	10.0	800	44.7	51.8	0.781	87.6
116	a ₃ -1	0.06	7.0	0	44.4	57.3	0.162	93.4
117	a ₃ -1	0.06	7.0	50	44.9	57.7	0.157	93.0
118	a ₃ -1	0.06	7.0	100	44.9	58.5	0.100	92.6
119	a ₃ -1	0.06	7.0	200	45.2	59.2	0.095	93.0
120	a ₃ -1	0.06	7.0	400	44.7	57.6	0.136	93.7
121	a ₃ -1	0.06	7.0	800	44.6	56.8	0.230	94.1
122	b ₃ -1	0.10	7.0	0	44.3	56.6	0.156	93.2
123	b ₃ -1	0.10	7.0	200	45.3	58.6	0.099	92.8
124	b ₃ -1	0.10	7.0	800	44.5	56.1	0.232	93.0
125	c ₃ -2	0.03	7.0	0	44.4	56.8	0.158	91.7
126	c ₃ -2	0.03	7.0	200	45.1	58.7	0.091	91.3
127	c ₃ -2	0.03	7.0	800	44.7	56.3	0.241	92.4

Note)

The Ca²⁺ ion concentrations in the above Table were determined in flotation.

According to the methods of Test Nos. 116 to 127 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound at a specific pH at a specific Ca^{2+} ion concentration, as compared with those of Test Nos. 110 to 115 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

Example III-15

Deinking test was carried out in a similar manner as that in Example I-9 except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table III-27 and that amphoteric compounds shown in Tables III-1, III-2 and III-3, and Table III-27 were used instead of the cationic compounds. For the adjustment of the Ca^{2+} ion concentration, CaCl_2 was used, and for the adjustment of Al^{3+} ion concentration, white water resulting from paper-making, or the white water and aluminum sulfate (in Test Nos. 131, 135 and 139) was(were) used. Further, for the adjustment of pH, hydrochloric acid or sodium hydroxide was used.

The results thereof are shown in Table III-27.

Table III-27

Test No.	Amphoteric compound		pH in flotation	Al ³⁺ ion conc. (ppm)	Ca ²⁺ ion conc. (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compd. No.	Amount added (%)				Before flotation	After flotation		
128	None	-	10.0	0	100	45.3	52.5	0.743	87.3
129	None	-	10.0	20	100	45.5	52.2	0.776	85.2
130	None	-	10.0	40	100	44.4	51.9	0.802	82.7
131	None	-	10.0	60	100	43.4	51.7	0.822	79.3
132	a ₃ -1	0.06	7.0	0	100	44.9	58.5	0.100	92.7
133	a ₃ -1	0.06	7.0	20	100	45.1	57.8	0.133	90.6
134	a ₃ -1	0.06	7.0	40	100	44.4	56.6	0.239	88.3
135	a ₃ -1	0.06	7.0	60	100	43.3	54.0	0.463	85.0
136	b ₃ -1	0.06	7.0	20	100	45.2	57.2	0.137	90.3
137	b ₃ -1	0.06	7.0	60	100	43.4	53.4	0.576	84.7
138	c ₃ -2	0.06	7.0	20	100	45.0	57.3	0.129	88.8
139	c ₃ -2	0.06	7.0	60	100	43.2	53.5	0.568	83.2

Note)

The Al³⁺ ion concentrations and the Ca²⁺ ion concentrations in the above Table were determined in flotation.

According to the methods of Test Nos. 132 to 139 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric

compound at a specific pH at a specific Ca^{2+} ion concentration, as compared with those of Test Nos. 128 to 131 (comparative methods), an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp there can be attained. Further, when Al^{3+} ion concentration of the slurry in flotation is 40 ppm or less, it can be expected to obtain qualities superior thereto.

Example III-16

Waste papers (news papers/leaflets = 75/25) recovered in a city were treated according to the following deinking methods, and the performances of the pulp sheet thus obtained were evaluated in the same manner as that in Example I-1. The results thereof are shown in Table III-28.

In this Example, the Ca^{2+} ion concentration of the warm water had been adjusted with CaCl_2 , while the Al^{3+} ion concentration thereof had been adjusted with white water resulting from paper-making.

(1) Test Nos. 140 and 141

The pulp sheet were prepared in a similar manner as that in Example I-10-(1) except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value

shown in Table III-28.

(2) Test Nos. 142 and 143

The pulp sheet were prepared in a similar manner as that in Example I-10-(2) except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table III-28. In Test No. 142, aluminum sulfate was also added to the pulp slurry to adjust the Al^{3+} concentration of the slurry to a value shown in Table III-28.

(3) Test Nos. 144 to 146

The pulp sheet were prepared in a similar manner as that in Example I-10-(3) except that the Al^{3+} ion concentrations, the Ca^{2+} ion concentrations and the pH of the pulp slurries were each adjusted to a value shown in Table III-28 and that amphoteric compounds shown in Tables III-1, III-2 and III-3, and Table III-28 were used instead of the cationic compounds.

Table III-28

Test No.	Nonionic compound or amphoteric compound	pH in flotation	Al ³⁺ ion conc. (ppm)	Ca ²⁺ ion conc. (ppm)	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Name or number of compound				Before flotation	After flotation		
140	None	4.5	30	5	42.2	52.9	0.683	87.8
141	None	7.0	15	200	42.1	52.8	0.690	87.1
142	NP-800	4.5	60	5	44.4	53.6	0.409	77.6
143	NP-800	7.0	15	200	44.6	53.4	0.418	78.2
144	a ₃ -1	7.0	15	200	45.3	58.3	0.113	90.3
145	b ₃ -5	7.0	15	200	45.4	58.2	0.118	90.1
146	c ₃ -5	7.0	15	200	45.3	57.9	0.120	89.7

Note)

The Al³⁺ ion concentrations and the Ca²⁺ ion concentrations in the above Table were determined in flotation.

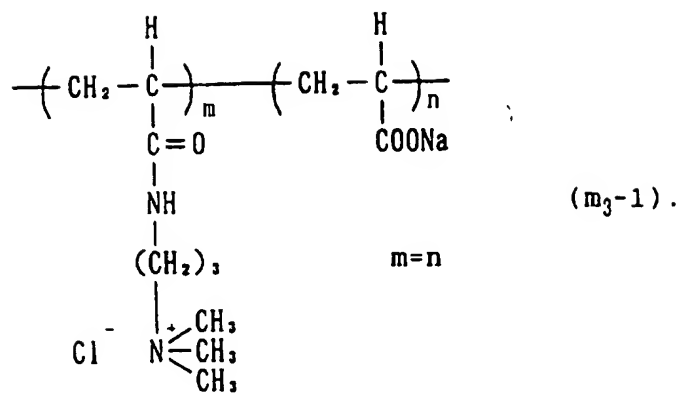
It is observed in Test Nos. 140 and 141 (comparative examples) that a lot of non-liberated ink spots which have not been removed from pulp by flotation is present in the reclaimed paper since the deinking agent having a poor power for liberating ink is used in the disintegrating step of waste papers. Accordingly, the reclaimed pulp is poor in quality. In Test Nos. 142 and 143 (comparative examples), the

addition of the polyacrylamide optionally with aluminum sulfate causes the re-adhesion of ink to cellulose fibers, and reduces the quality of the reclaimed pulp. Further, it is observed that foaming in flotation is extremely enhanced to deteriorate the recovery of pulp.

In contrast, according to the methods of Test Nos. 144 to 146 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound at a specific pH at a specific Ca^{2+} ion concentration and at a specific Al^{3+} ion concentration, an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp are observed.

Example III-17

Deinking test was carried out according to the method described in Example III-1 by using amphoteric compound m₃-1 represented by the following formula:



The results are shown in Table III-14.

Table III-29

Test No.	Amphoteric polymer				pH in flotation	Whiteness (%)		Residual ink area ratio (%)	Recovery of pulp (%)
	Compd. No.	Content of cationic nitrogen* (%)	weight-average molecular weight	Amount added (%)		Before flotation	After flotation		
147	None	-	-	-	10.0	45.0	52.2	0.752	86.8
148	None	-	-	-	9.0	45.4	52.8	0.683	87.2
149	None	-	-	-	8.0	44.9	53.3	0.411	88.3
150	None	-	-	-	7.0	45.6	53.6	0.365	88.9
151	None	-	-	-	6.0	45.0	54.0	0.329	88.9
152	None	-	-	-	5.0	44.6	53.1	0.431	89.1
153	None	-	-	-	4.0	44.3	52.9	0.625	87.6
154	μ_3 -1	4.65	15,000	0.01	9.0	44.8	55.7	0.264	87.1
155	μ_3 -1	4.65	15,000	0.01	8.0	45.0	57.7	0.145	89.3
156	μ_3 -1	4.65	15,000	0.01	7.0	45.2	58.1	0.138	90.2
157	μ_3 -1	4.65	15,000	0.01	6.0	44.8	57.8	0.148	89.5
158	μ_3 -1	4.65	15,000	0.01	5.0	44.7	57.3	0.167	89.4
159	μ_3 -1	4.65	15,000	0.01	4.0	44.8	56.7	0.231	88.3

Note)

*: The content (%) of cationic nitrogen was calculated by multiplying the nitrogen content (%) determined by Kjeldahl method by the ratio of the cationic nitrogen to the total nitrogen which was determined from the molecular formula of the polymer.

In the tests described above, Test No. 147 is effected in a similar manner as that of a conventional industrial deinking method. According to the methods of Test Nos. 154 to 159 (the methods of the present invention) wherein the flotation is effected in the presence of an amphoteric compound at a specific pH, as compared with those of Test Nos. 147 to 153 (comparative methods), there can be expected to attain an improvement in whiteness of the reclaimed paper, a reduction of residual ink spots in the reclaimed paper and an increase in the recovery of pulp, by the selective removal of ink in flotation.

CLAIMS

1. A deinking method comprising the steps of liberating ink from waste paper as a raw material and removing the liberated ink from a flotation system, which comprises adding at least one nonionic surfactant for liberating ink from said waste paper; adjusting the pH of a system to pH 4 to 9 before or during said step for removing the liberated ink from a flotation system; and adding at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds before or during said step for removing the liberated ink from a flotation system.

2. The deinking method according to Claim 1, wherein said nonionic surfactant is selected from the group consisting of nonionic surfactants (A) to (D):

nonionic surfactant (A): a reaction product obtained by adding an alkylene oxide to a mixture of an oil & fat and an alcohol.

nonionic surfactant (B): a compound represented by the formula: $\text{RCOO}(\text{AO})_n\text{R}'$ (wherein R represents an alkyl or alkenyl group having 7 to 23 carbon atoms; R' represents a hydrogen atom, an alkyl group having 1 to 22 carbon atoms, an alkenyl group having 2 to 22

carbon atoms, or an acyl group having 2 to 22 carbon atoms; AO represents an oxyalkylene group having 2 to 4 carbon atoms; and m is an integer of 1 or more),

nonionic surfactant (C): a compound represented by the formula: $RO(AO)_nH$ (wherein R represents an alkyl or alkenyl group having 8 to 24 carbon atoms; AO represents an oxyalkylene group having 2 to 4 carbon atoms; and n is an integer of 1 or more), and

nonionic surfactant (D): a reaction product obtained by adding an alkylene oxide to a polyvalent carboxylic acid or an acid anhydride thereof; or a reaction product obtained by adding an alkylene oxide to a mixture of a polyvalent carboxylic acid or an acid anhydride thereof, and alcohol.

3. The deinking method according to Claim 1, which comprises maintaining the calcium ion concentration of the flotation system at a concentration of from 10 to 400 ppm.

4. The deinking method according to Claim 3, wherein said calcium ion concentration of the flotation system is from 100 to 250 ppm.

5. The deinking method according to Claim 1, which comprises maintaining the aluminum ion concentration of the flotation system at a concentration of from 0 to 40 ppm.

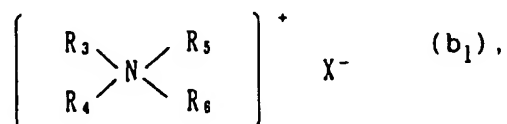
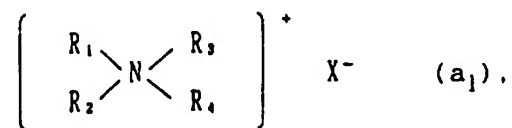
6. The deinking method according to Claim 1, which comprises adding at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds to the flotation system after adjusting the pH of the system to a value in a range of from pH4 to pH9.

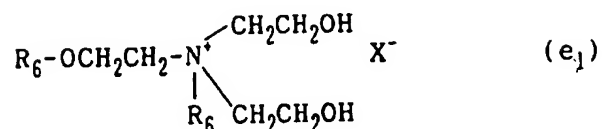
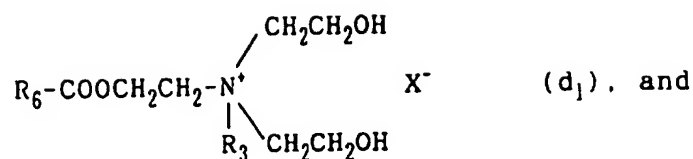
7. The deinking method according to Claim 6, which comprises adding at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds in an amount such that the pH of the flotation system is scarcely altered by the addition of such at least one member.

8. The deinking method according to Claim 6, which comprises adding at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds in an amount of from 0.01 to 1.0% by weight based on the weight of the waste paper.

9. The deinking method according to Claim 1, wherein the cationic compounds are selected from the group consisting of compounds represented by the following formulas (a₁) to (e₁) and cationic polymers represented by the following formulas (f₁) to (j₁) each of which has a cationic nitrogen content of 0.01 to

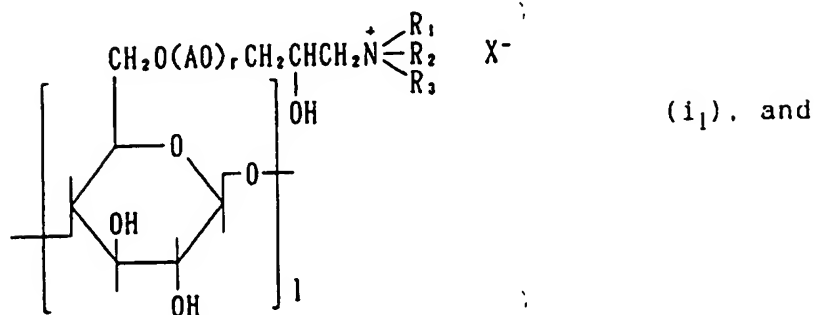
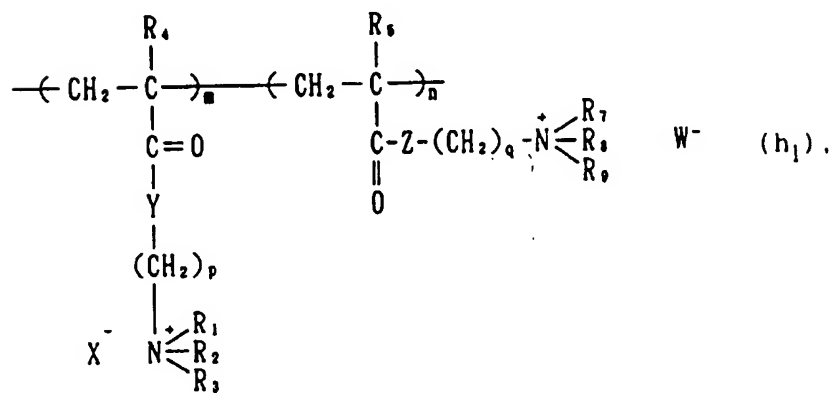
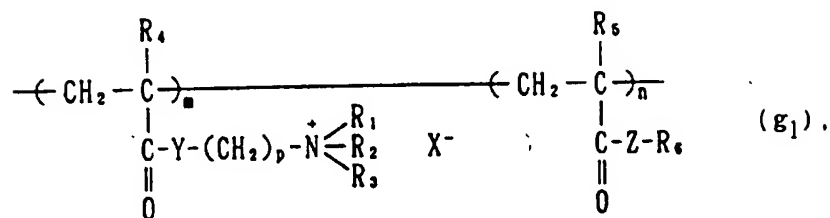
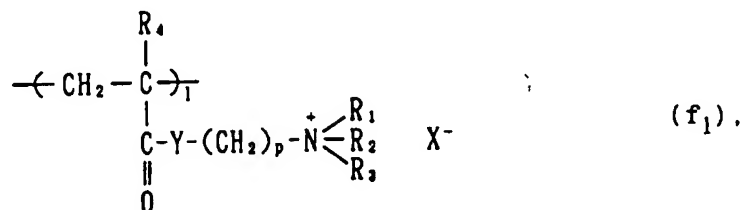
35% by weight and a weight-average molecular weight of 2,000 to 3,000,000; the amines and acid salts of amines are selected from the group consisting of compounds represented by the following formulas (a₁) to (h₂) and polymers represented by the following formulas (i₂) to (l₂) each of which has an amino-nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000; and the amphoteric compounds are selected from the group consisting of compounds represented by the following formulas (a₃) to (j₃), phospholipids (k₃), proteins (l₃) and amphoteric polymers represented by the following formulas (m₃) and (n₃) each of which has a cationic nitrogen content of 0.01 to 35% by weight and a weight-average molecular weight of 2,000 to 3,000,000:

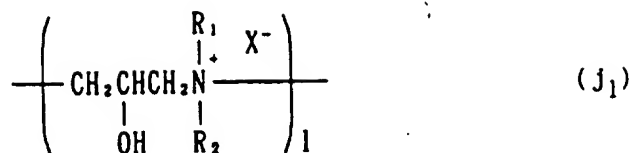




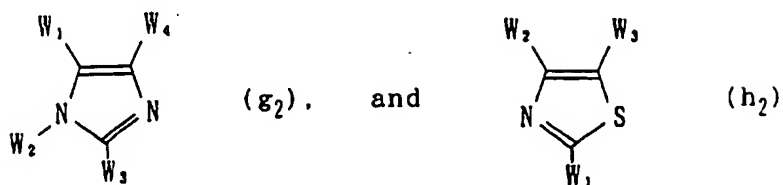
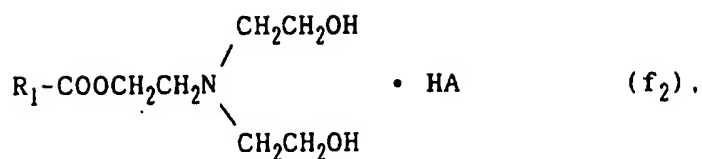
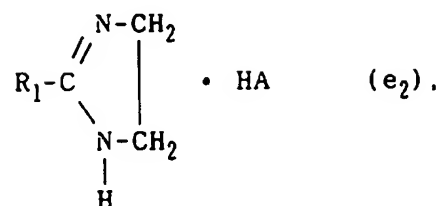
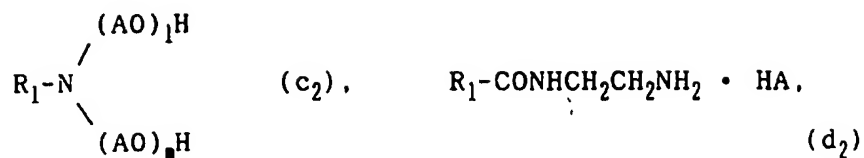
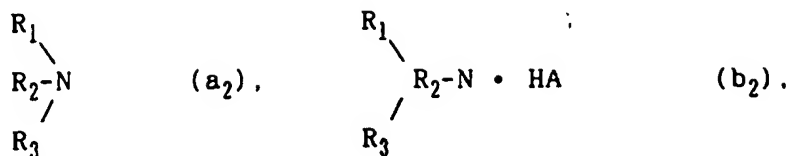
in formulas (a₁) to (e₁), R₁ and R₂ may be the same or different from each other and each represents an alkyl, alkenyl or β-hydroxyalkyl group having 10 to 24 carbon atoms; R₃, R₄ and R₅ may be the same or different from one another and each represents an alkyl or hydroxyalkyl group having 1 to 8 carbon atoms, a benzyl group, or a group represented by the formula: -(AO)_n-Z (wherein AO represents an oxyalkylene group having 2 to 4 carbon atoms, Z represents a hydrogen atom or an acyl group, and n is an integer of from 1 to 50); R₆ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; X⁻ represents a counter ion; and Y represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms, a group represented by the formula: R₆COOCH₂- (wherein R₆ is as defined above), a group represented by the

formula: $R_6\text{CONHCH}_2-$ (wherein R_6 is as defined above) or a group represented by the formula:
 $R_6\text{OCH}_2-$ (wherein R_6 is as defined above);



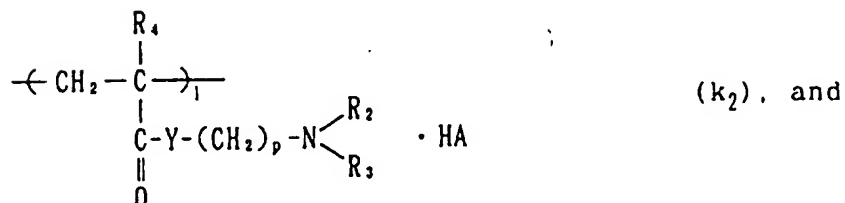
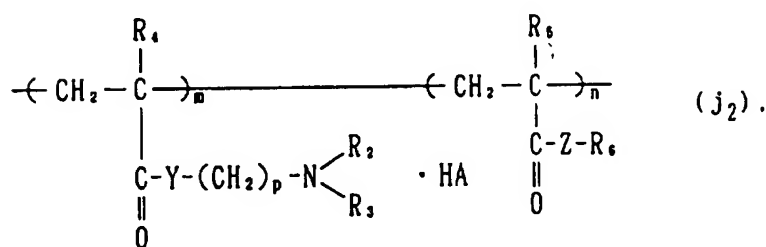


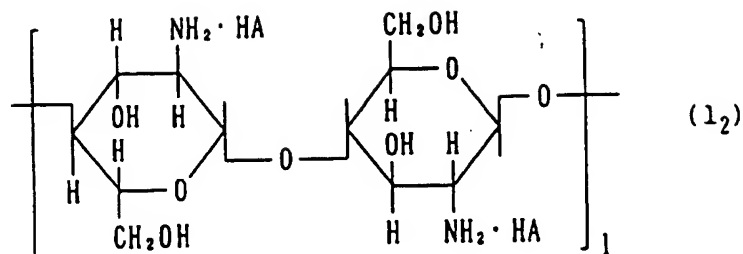
in formulas (f₁) to (j₁), R₁, R₂, R₃, R₆, R₇, R₈ and R₉ may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ and R₅ may be the same or different from each other and each represents a hydrogen atom or a methyl group; X⁻ and W⁻ may be the same or different from each other and each represents a counter ion; Y and Z may be the same or different from each other and each represents O or NH; A0 represents an oxyalkylene group having 2 to 4 carbon atoms; p and q may be the same or different from each other and each represents an integer of 1 to 10; r represents an integer of 0 to 10; and l, m and n are each such a positive number that the weight-average molecular weight of the polymer would be a value in the range of from 2,000 to 3,000,000;



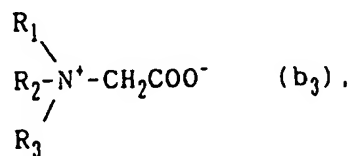
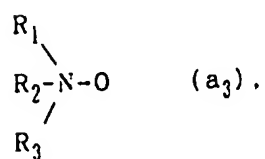
in formulas (a₂) to (h₂), R₁ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; R₂ and R₃ may be the same or different from each other and each represents a

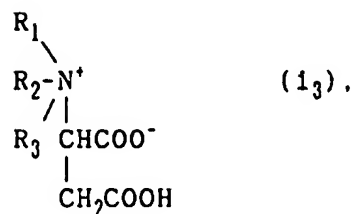
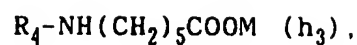
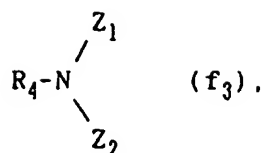
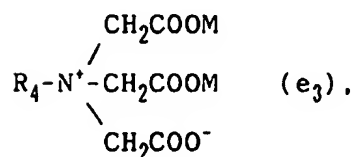
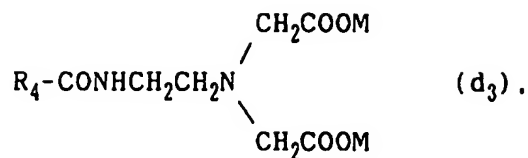
hydrogen atom, an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; HA represents an inorganic or organic acid; AO represents an oxyalkylene group having 2 to 4 carbon atoms; l and m are each zero or a positive integer with the proviso that l plus m is an integer of 1 to 300; and W_1 , W_2 , W_3 and W_4 may be the same or different from one another and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms;



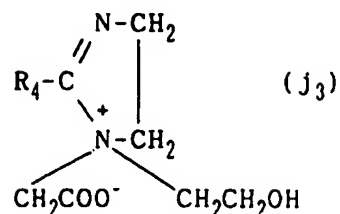


in formulas (1₂) to (1₂). R₁ represents an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₂, R₃ and R₆ may be the same or different from one another and each represents a hydrogen atom, an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ and R₅ may be the same or different from each other and each represents a hydrogen atom or a methyl group; HA represents an inorganic or organic acid; Y represents O or NH; p represents an integer of 1 to 10; and l, m and n are each such a positive number that the weight-average molecular weight of the polymer would be a value in the range of from 2,000 to 3,000,000;



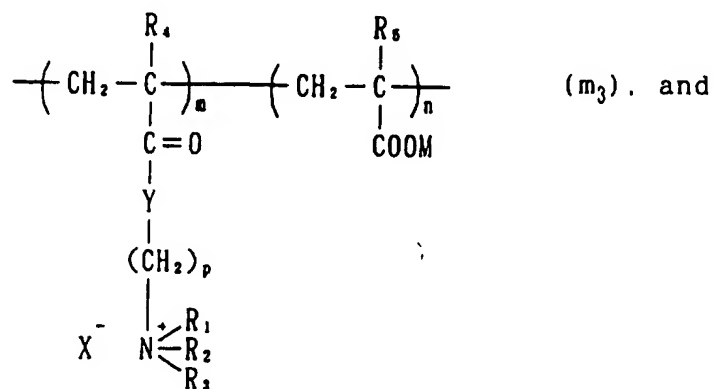


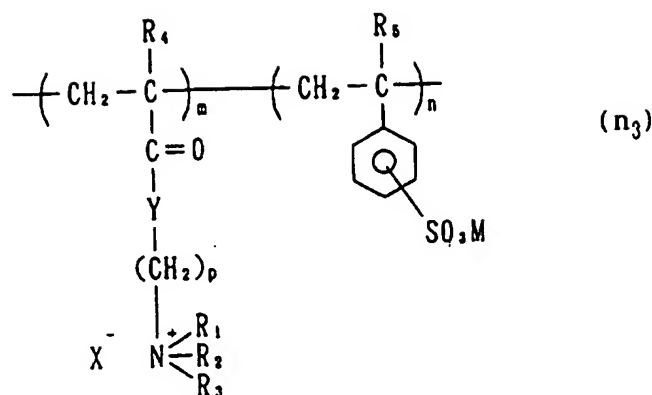
and



in formulas (a₃) to (j₃), R₁, R₂ and R₃ may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ represents an alkyl, alkenyl or β-hydroxyalkyl group having 8 to 36 carbon atoms; M represents a hydrogen atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an

ammonium group; Y_1 represents a group represented by the formula: $R_5NHCH_2CH_2-$ (wherein R_5 represents an alkyl group having 1 to 36 carbon atoms or an alkenyl or β -hydroxyalkyl group having 2 to 36 carbon atoms); Y_2 represents a hydrogen atom or a group represented by the formula: $R_5NHCH_2CH_2-$ (wherein R_5 is as defined above); Z_1 represents a group represented by the formula: $-CH_2COOM$ (wherein M is as defined above); and Z_2 represents a hydrogen atom or a group represented by the formula: $-CH_2COOM$ (wherein M is as defined above); and

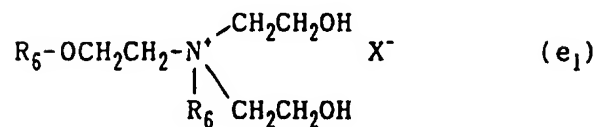
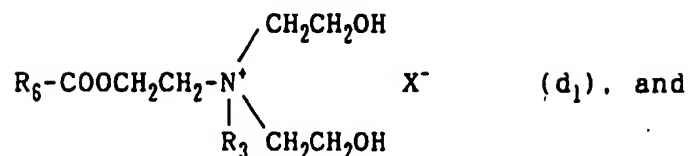
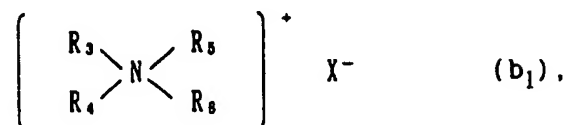
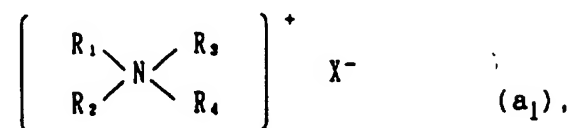




in formulas (m₃) and (n₃). R₁, R₂ and R₃ may be the same or different from one another and each represents a hydrogen atom, an alkyl group having 1 to 24 carbon atoms or an alkenyl group having 2 to 24 carbon atoms; R₄ and R₅ may be the same or different from each other and each represents a hydrogen atom or a methyl group; M represents a hydrogen atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an ammonium group; X⁻ represents a counter ion; Y represents O or NH; p is an integer of 1 to 10; and m and n are each such a positive number that the weight-average molecular weight of the polymer would be a value in the range of from 2,000 to 3,000,000.

10. The deinking method according to Claim 2, wherein at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds is selected among

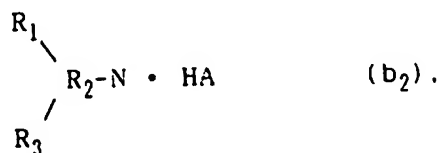
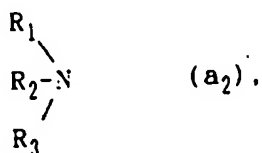
cationic compounds represented by the following formulas (a₁) to (e₁):

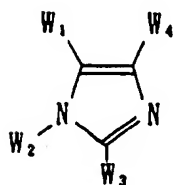
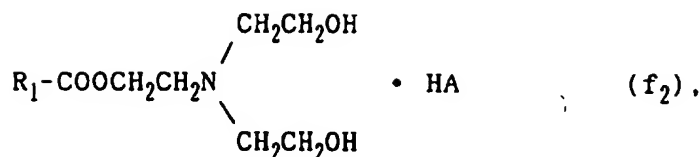
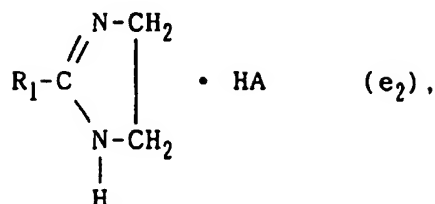
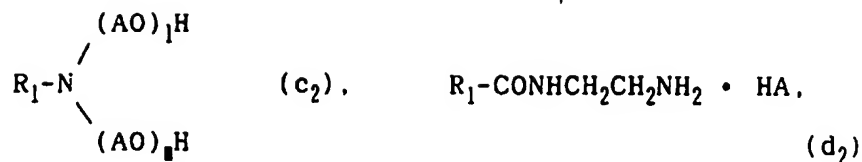


wherein R₁ and R₂ may be the same or different from each other and each represents an alkyl, alkenyl or β-hydroxyalkyl group having 10 to 24 carbon atoms; R₃, R₄ and R₅ may be the same or different from one another and each represents an alkyl or hydroxyalkyl group having 1 to 8 carbon

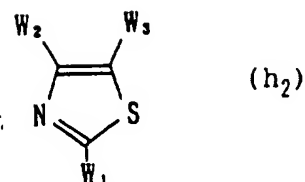
atoms, a benzyl group, or a group represented by the formula: $-(AO)_n-Z$ (wherein AO represents an oxyalkylene group having 2 to 4 carbon atoms, Z represents a hydrogen atom or an acyl group, and n is an integer of from 1 to 50); R_6 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms; X^- represents a counter ion; and Y represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms, a group represented by the formula: $R_6COOCH_2^-$ (wherein R_6 is as defined above), a group represented by the formula: $R_6CONHCH_2^-$ (wherein R_6 is as defined above) or a group represented by the formula: $R_6OCH_2^-$ (wherein R_6 is as defined above).

11. The deinking method according to Claim 2, wherein at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds is selected among amines and acid salts of amines represented by the following formulas (a₂) to (h₂):





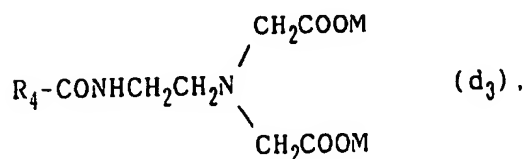
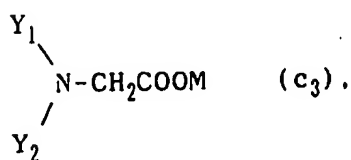
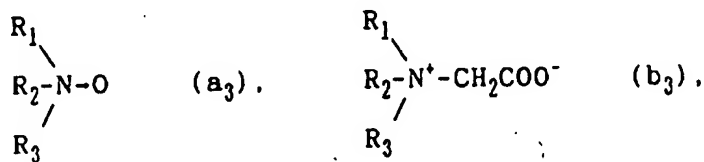
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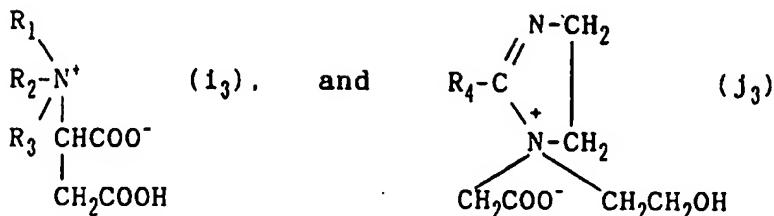
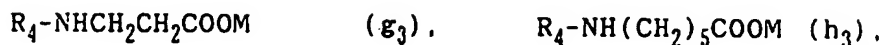
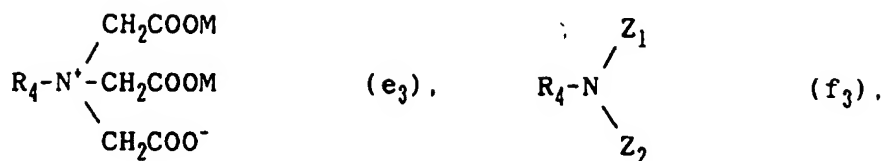


wherein R_1 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms; R_2 and R_3 may be the same or different from each other and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms; HA represents an inorganic or organic acid; AO represents an oxyalkylene group having 2 to 4 carbon atoms; l and m are each such an integer

that 1 plus m would be a numerical value of above zero and 300 or below; and W_1 , W_2 , W_3 and W_4 may be the same or different from one another and each represents a hydrogen atom or an alkyl group having 1 to 24 carbon atoms.

12. The deinking method according to Claim 2, wherein at least one member selected from the group consisting of cationic compounds, amines, acid salts of amines and amphoteric compounds is selected among amphoteric compounds represented by the following formulas (a₃) to (j₃), phospholipids (k₃) and proteins (l₃):





wherein R_1 , R_2 and R_3 may be the same or different from one another and each represents an alkyl group having 1 to 24 carbon atoms; R_4 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms; M represents a hydrogen atom, an alkali metal atom, 1/2 mole of an alkaline earth metal atom or an ammonium group; Y_1 represents a group represented by the formula: $R_5\text{NHCH}_2\text{CH}_2-$ (wherein R_5 represents an alkyl, alkenyl or β -hydroxyalkyl group having 8 to 36 carbon atoms); Y_2 represents a hydrogen atom or a group represented by the formula: $R_5\text{NHCH}_2\text{CH}_2-$ (wherein R_5 is as defined above); Z_1 represents a group represented by the formula: $-\text{CH}_2\text{COOM}$ (wherein M is as defined above); and Z_2 represents

a hydrogen atom or a group represented by the
formula: $-\text{CH}_2\text{COOM}$ (wherein M is as defined above).

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/JP 96/00942

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21C5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,94 28237 (HIGH POINT CHEMICAL CORP) 8 December 1994 see page 4 - page 8; claim 1	1,2
Y	see the whole document	1,2,6-9
Y	WO,A,93 21376 (ALLIED COLLOIDS LTD ;LANGLEY JOHN GRAHAM (GB)) 28 October 1993 see page 6, line 1 - page 8, line 27; claims 1,10	1,2
P,X	EP,A,0 657 578 (PAPIERFABRIK UTZENSTORF AG ;W KOLB AG DR (CH)) 14 June 1995 see the whole document	1,2
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *&* document member of the same patent family

Date of the actual completion of the international search

4 July 1996

Date of mailing of the international search report

29.07.96

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Fax (+ 31-70) 340-3016

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INTERNATIONAL SEARCH REPORT

Int. Jonal Application No

PCT/JP 96/00942

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 12026 (ALLIED COLLOIDS LTD ;STOCKWELL JOHN OLIVER (GB); BINGHAM TIMOTHY G) 4 May 1995 see page 8, line 7 - page 8, line 8; claims 1,3,4 ---	1,6-11
Y	DATABASE WPI Week 7913 Derwent Publications Ltd., London, GB; AN 79-24833B XP002007473 & JP,A,54 023 705 (HONSHU PAPER MFG KK) , 22 February 1979 cited in the application see abstract ---	1,2,6-9
A	GB,A,2 125 058 (ECONOMICS LAB) 29 February 1984 see claim 12; example 2 & JP,A,59 053 532 cited in the application ---	1
A	US,A,4 043 908 (ROBERTS KELVIN ET AL) 23 August 1977 cited in the application ---	
A	US,A,4 162 186 (MCLAUGHLIN ROBERT L ET AL) 24 July 1979 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 96/00942

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO-A-9321376	28-10-93	AU-B- 3902993 CA-A- 2118304 EP-A- 0636192 FI-A- 944826 JP-T- 7505683 NO-A- 943916 ZA-A- 9302615	18-11-93 28-10-93 01-02-95 13-10-94 22-06-95 14-10-94 14-04-94
EP-A-0657578	14-06-95	DE-A- 4443229	08-06-95
WO-A-9512026	04-05-95	AU-B- 7997894 BR-A- 9406216 EP-A- 0680530 FI-A- 953087 NO-A- 952568 PL-A- 309626 ZA-A- 9408463	22-05-95 09-01-96 08-11-95 16-08-95 22-08-95 30-10-95 27-10-95
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US-A-4043908	23-08-77	SE-B- 406482 AT-B- 357862 AU-B- 504797	12-02-79 11-08-80 01-11-79

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 96/00942

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		FR-A,B 2313500	31-12-76
		GB-A- 1546813	31-05-79
		JP-A- 52031563	10-03-77
		NL-A- 7602000	14-09-76
		SE-A- 7502720	13-09-76

US-A-4162186	24-07-79	NONE	
